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METALLURGY.

THE ART OF EXTRACTING METALS FROM THEIR ORES,
AND ADAPTING THEM TO VARIOUS PURPOSES
OF MANUFACTURE.

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FUEL; FIRE-CLAYS; COPPER; ZINC; BRASS, ETC.

WITH ILLUSTRATIONS CHIEFLY FROM ORIGINAL DRAWINGS,
CAREFULLY LAID DOWN TO SCALE.

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TO

MICHAEL FARADAY,

WITH THE SINCERE RESPECT

AND

AFFECTIONATE REGARD

OF

THE AUTHOR

PREFACE.

In no country are the operations of Metallurgy conducted on so vast a scale as in Great Britain; and yet the contributions which have been made to the literature of the subject by British metallurgists are few and scanty in the extreme. But this should not lead to the erroneous conclusion which some persons are inclined to draw, that our smelters are too ignorant of chemistry to understand the theory of the processes under their direction, or too illiterate to be able to record the results of their experience. I have the pleasure of knowing many of these men intimately, and I will venture to affirm that with respect to knowledge, both of the theory and practice of the special departments of the Art in which they are engaged, they are not excelled by any metallurgists in Europe.

The chief writers on Metallurgy are the Germans, to whom we owe two of the most remarkable works on the subject, namely, the treatise of Agricola, in Latin, which appeared in 1555; and the System of Metallurgy of Karsten, in German, published in 1831. The monographs, contributions to periodicals, and compendious treatises relating to the science and practice of Metallurgy which have been published in the German language, are very numerous. We are, probably, indebted to the Germans, to a greater extent than is commonly supposed, for the development of our mineral resources, since the introduction of German miners and metallurgists into England, about three centuries ago, through the wisdom of Elizabeth.

The Swedes, who, in the persons of Scheele and Berzelius, have played so distinguished a part in raising chemistry to the dignity of a science, have not been behind with respect to Metallurgy. Many valuable monographs and original papers on metallurgical subjects exist in the Swedish language, which unfortunately is but little known to Englishmen. The 'Jern-Kontorets Annaler,' or Annals of the Board of Iron-Masters, now consist of about forty volumes, which contain theoretical and practical papers of the highest interest to Miners and Metallurgists.

The French have published extensively on metallurgical subjects; and the 'Annales des Mines' form a repertory of metallurgical knowledge of great value. The chief contributors to this work have been the graduates and students of the École des Mines; and their contributions, to a large extent, consist of the descriptions of processes which they have witnessed out of France. It is not a little surprising, that, considering the skill in arrangement and the precision of language which usually distinguish French scientific writers, no complete treatise of Metallurgy should yet have appeared in France.

In the exercise of my duties as Lecturer on Metallurgy at the Government School of Mines, during the last ten years, I have constantly felt the want of a comprehensive treatise on the subject in the English language, to which I might refer the students; and I have heard repeated expressions of regret from many of our practical Metallurgists that no such treatise existed. I now attempt to supply this deficiency; and it is only after some years of deliberation that I decided to take this step. It is obvious that a work of this kind must be in great measure a compilation; nevertheless, through the following pages will be found interspersed original analyses, and the results of numerous experiments and investigations, which are now published for the first time.

I may be permitted to state that, although educated for the profession of Medicine, and for some years engaged in the actual practice of it, I long ago acquired a strong predilection for the study of Metallurgy, to which I have almost exclusively devoted my attention during the last twenty years. I have availed myself of every opportunity of visiting metallurgical works, and have recorded the results of my observations; but I have never entered an establishment without the consent either of the proprietor or of the responsible manager; and never will I disclose what I have witnessed, or what may have been communicated to me in confidence, without the fullest authority to do so.

The method of arrangement which I have adopted in this work is nearly the same as that which I have followed in my lectures. So far as relates to the instruction of students, it has, I believe, succeeded. It is almost a matter of indifference in what order the metals are considered; for, with few exceptions, the metallurgy of each metal forms a subject distinct, independent, and complete in itself.

The descriptions of nearly all the processes occurring in this volume have been revised in type by the managers of the various works; and in every case I have been careful to specify the names of those gentlemen who have thus rendered me such essential service. Amongst foreign metallurgists, my thanks are most especially due to those of Sweden for their prompt and hearty co-operation.

It affords me much pleasure to acknowledge my obligations to the friends who have assisted me in my investigations. While this is only an act of simple justice, it is also one of policy; for men work with a much better heart when they know that the credit of their labours will not be appropriated by others without acknowledgment.

I cannot refrain from mentioning in this place the name of one friend, who has rendered me most willing, and I may add, most valuable aid,—it is that of my colleague Mr. Richard Smith. The descriptions of the methods of assaying the ores of copper and zinc are by Mr. Smith, who has been almost daily occupied, during the last ten years, in instructing students in the art of assaying.

I must not pass over in silence the names of the engraver and draughtsman—Mr. James Cooper and Mr. Richard W. Mallett. They have entered heartily upon their task. I impressed upon them that their first consideration should be accuracy; and I believe they have succeeded in producing wood-engravings which, in that respect, can hardly be surpassed. The illustrations for the second volume, especially those relating to Iron, will exemplify the skill of these artists in a far more striking manner than any contained in this. The woodcuts might have been made more attractive to the eye by the free use of shadows, or by means of perspective; but I believe that they would have been thereby rendered less useful to practical men. As it is, almost every woodcut may be regarded as an accurate, though small, mechanical drawing; and it is only measurable drawings of this kind which are of real utility in practice.

I have taken every precaution in my power to avoid errors; and yet doubtless some—I hope not many—will have escaped detection. I shall be obliged to any one who, in the course of reading this volume, may discover errors, to communicate with me on the subject.

This work will be completed in one more volume, containing the

subjects of Iron, Lead, Silver, Gold, Platinum, Nickel, Cobalt, Arsenic, Bismuth, Antimony, Tin, Mercury, etc. Nearly the whole of the material for this volume is collected, and almost all the illustrations are executed, so that I hope it will be ready for publication before the end of 1862.

GOVERNMENT SCHOOL OF MINES,

London, Nov. 1861.

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METALLURGY.

INTRODUCTION.

METALLURGY, as at present understood, is the art of extracting metals from their ores, and adapting them to various purposes of manufacture.

The etymology of the word "metallurgy" (*μέταλλον*, *ore*, *metal*, and *ἔργον*, *work*) would seem to imply a more extended meaning, and to include all the arts in which metals are wrought into objects of utility or ornament; but this is not the present meaning of the word.

It is the province of the miner to extract ores from the earth, and by the mechanical processes of *dressing* to free them more or less completely from foreign matter, and so render them fit for treatment by the metallurgist.

The knowledge of the principles of metallurgy is the science of metallurgy. And as the phenomena observed in metallurgical processes relate to physics and chemistry, and as mechanical appliances of various kinds are employed in these processes, it follows that the sciences of chemistry, physics, and mechanics must be the foundation of the science of metallurgy. In order, therefore, that the student may with advantage enter upon the study of metallurgy, it is essential that he should possess a considerable amount of preliminary knowledge.

As the word science in relation to a manufacturing art is often vaguely used, it may be well to give the following illustration of its meaning. When an ore of copper, consisting essentially of copper, iron, sulphur, and silica, is subjected to a series of processes, such as heating with access of air under special conditions, melting, &c., copper is separated in the metallic state. The sum of these processes is termed the smelting of copper. In this operation of smelting, certain chemical changes take place: the sulphur combines with the oxygen of the air, and is evolved chiefly as sulphurous acid; the iron is similarly converted into oxide, which combines with the silica present to form a fusible compound or slag. There are thus several facts which are proved on chemical evidence. These facts, when systematically arranged, may be said to constitute the scientific knowledge of copper-smelting; and that knowledge implies necessarily a knowledge of the chemical relations of copper, iron, sulphur, oxygen, and silica to each other. There are many other facts connected with copper-smelting, but those mentioned suffice for the present purpose of illustration. The man who conducts the process of copper-smelting in ignorance of these facts, has simply an empirical, in contradistinction to a scientific, knowledge of the art.

The history of metallurgy dates from the remotest antiquity; and, as Le Play correctly observes, "most of the fundamental phenomena of metallurgy were discovered and regularly applied to the wants of man before the physical sciences properly so called existed."[1]

The term metal, like the term acid, is rather conventional than strictly scientific. Formerly, when science was much less advanced than at present, the metals constituted a well-defined class of elements. The properties which were regarded as specially characteristic were physical, and were not founded on chemical relations. Thus lustre, *sui generis*, and high specific gravity were considered to be essential characters of all metals. But we are now acquainted with metals which have a lower specific gravity than water, and with non-metallic elements which present a strong metallic lustre: sodium and lithium are examples of the former, while carbon in the state of graphite and a variety of crystallized silicon are examples of the latter.

By far the greater number of the elementary bodies at present known are metals.

ON CERTAIN PHYSICAL PROPERTIES OF METALS.

PHYSICAL STATE.—They are all solid, excepting mercury, at the ordinary temperature of the atmosphere.

Action of Heat.—The following is a convenient practical classification of the metals, founded on their degree of fusibility:[2]—

a. *Fusible below redness.*—Tin, lead, &c.

b. *Fusible above redness, but at temperatures easily attainable in furnaces.*—Copper, gold, &c.

c. *Fusible only at the highest temperatures attainable in furnaces.*—Nickel, manganese, &c.

d. *Practically infusible, at least in ordinary furnaces.*—Platinum, iridium, &c.

Unfortunately there is no instrument by which high temperatures can be accurately and readily measured. The ordinary language employed to indicate high temperatures, such as red heat, white heat, &c., is very unsatisfactory, as, in judging of temperature by the eye, much may depend upon the observer as well as upon the degree of illumination under which the observation is made.

Pouillet has employed an air-thermometer provided with a bulb of platinum to determine with precision high degrees of temperature; and by this means he has arrived at the following results:[3]—

---

[1] Description des Procédés Métallurgiques employés dans le Pays de Galles pour la fabrication du Cuivre. Paris, 1848.

[2] Mr. Hopkins, of Cambridge, has shown that, when certain metals and other bodies are subjected to great pressure, they require a higher temperature for fusion. Brit. Assoc. 1854.

[3] Comptes Rendus, 1836, 3, p. 782.

Incipient red heat corresponds to	525° C.	977° F.
Dull red	„	700	1292
Incipient cherry red	„	800	1472
Cherry red	„	900	1652
Clear cherry red	„	1000	1832
Deep orange	„	1100	2012
Clear orange	„	1200	2192
White	„	1300	2372
Bright white	„	1400	2552
Dazzling white	„	1500 to 1600	2732 to 2912

Metals are either *fixed* or *volatile by heat.*

a. *Fixed metals.*—Gold, copper, nickel, &c.

b. *Volatile metals.—After fusion:*—Cadmium, zinc, &c.; *without fusion, passing directly from the solid to the gaseous state:*—Arsenic.

It is important to remark that the term *fixed* is necessarily comparative and conventional. A metal, which may be considered as practically fixed, may yet be volatilized at very high temperatures, such as are attained by concentrating the solar rays in the focus of a mirror or lens, by the voltaic current, or by the combustion of oxygen and hydrogen.

M. Despretz has published some interesting experiments on the production of intense heat, by employing in conjunction the heat derived from the solar rays, the oxy-hydrogen blowpipe, and a powerful [illegible]taic battery. By this triple source of heat, magnesia, it is stated, [illegible] immediately volatilized in the form of white vapour, and anthra[illegible]elted. By the action of a very powerful Bunsen's battery alone, [illegible]carbon was melted, volatilized, and condensed in the state of a [illegible] crystalline powder; silicon, boron, titanium, and tungsten were [illegible]d; and 250 grms. (3858 grs.) of cuttings of platinum were melted [illegible] few minutes.[4] Deville and Debray have recently succeeded in [illegible]ing not less than 25 kilogrammes (55 lbs. avoird,) of platinum at a [illegible]e by the heat resulting from the combustion of coal-gas by oxygen.[5] [illegible]ron becomes soft, and remains so, through a considerable range [illegible]temperature below its fusing-point. In this soft state two pieces [illegible]iron may be made to unite by compression, or, in other words, may [illegible] welded together. In the process of welding the metal is never in [illegible]tate of absolute fusion.

[illegible]PECIFIC GRAVITY.—The specific gravity of metals at the ordinary [illegible]perature ranges between 0·6[6] and 21·5.[7] It varies within certain [illegible]ts with the special molecular condition of the metal consequent on [illegible]ious treatment.[8] The processes of hammering, rolling, and [illegible]pping tend to increase the specific gravity of metals in the state [illegible]which they exist after fusion. Marchand, however, asserts that

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[illegible] Comptes Rendus, t. 28, p. 755; t. 29, [illegible]48, 545, 709.

[illegible] Ibid., t. 50, p. 1038. June, 1860.

[illegible] Sp. gr. of lithium as determined by [illegible]nsen.

[7] Sp. gr. of fused platinum, Deville, Ann. de Chim. et de Phys. 1859, 3. s. 56, p. 420.

[8] Vid. specific gravity of copper in the sequel.

bismuth is an exception, and that by subjecting the metal to great pressure its specific gravity is diminished. But Dr. Tyndall informs me that he has not been able to verify this assertion by experiment with a small hydraulic press. In recording the specific gravity of a metal, it is important in every case to specify the treatment which it may have previously received, as well as the temperature at which the observation was made; for otherwise the results of different observers cannot be satisfactorily compared.

CRYSTALLIZATION.—The brittle metals in common use always exhibit a well-marked crystalline structure. This is especially the case with zinc, antimony, and bismuth, upon the fractured surfaces of which distinct crystalline faces may be seen. The soft metals, such as lead and tin, may also be readily obtained well crystallized.

The metals, so far as observations have extended, have been found to crystallize either in the *cubic* or *rhombohedral* systems: thus gold, silver, lead, and copper occur either in cubes, the regular octahedron or rhombic dodecahedron; while bismuth, which was long supposed to crystallize in cubes, belongs to the rhombohedral system.

The conditions under which metals generally crystallize are as follow:—

a. *On solidification after fusion.*

b. *By condensation from the state of vapour.*

c. *By electrolytic decomposition of metallic solutions.*

a. *Solidification after fusion.*—Slowness of cooling is, as migl
expected, the condition favourable to crystallization. Thus an
of zinc, when allowed to cool very slowly, presents much l
crystalline faces on the fractured surface than when cooled qu
The same fact is also strikingly exemplified in grey pig-iron w
similarly treated. If one portion of this metal be allowed to
from a furnace upon a cold slab of iron, so as to be cooled with
treme rapidity, and another portion be allowed to run under a mass
hot slag, so as to be cooled with extreme slowness, the fracture of
latter will be much more largely crystalline than that of the former;
much so that it may be difficult to believe that the two portions of me
should have flowed simultaneously from the same furnace.

When it is desired to prepare a metal in a well-crystallized st
after fusion, the usual process is to melt a considerable quantity
it in a crucible, and when the surface has solidified to a slight de
to break the crust, and as rapidly as possible pour out the still li
metal. Pure bismuth may be thus procured in beautiful crystals;
some dexterity is required to perform the operation successfully
have beautiful specimens of copper, brass, and pig-iron, which h
been accidentally crystallized on this principle.

When melted lead is allowed to cool slowly, and is stirred fi
time to time, a period arrives when, owing to its partial solidificat
in the form of small crystals, it becomes a semi-fluid mass. T
crystals, which have a higher specific gravity than the liquid me

and consequently tend to subside, may be taken out and drained by means of an iron ladle perforated with holes. This is actually done on the large scale, as will be described in the sequel, in the well-known process of Pattinson. Crystals of tin may be obtained in a similar manner with equal facility. If the lead had been allowed to solidify without being disturbed, it would have presented no visible evidence of crystallization, and yet it must have consisted of an aggregation of crystals.

It seems reasonable to suppose that while slow cooling is favourable to crystallization, extremely rapid cooling may, in some instances at least, determine a non-crystalline condition, or a molecular arrangement similar to that of bodies in the vitreous state.

b. *Condensation from vapour.*—When arsenic is volatilized, it condenses in the form of a crystalline crust. The vapour of zinc may likewise condense in a distinctly crystalline form.

c. *Electrolytic decomposition.*—Metals which may be separated in the metallic state from a solution of their salts by the voltaic current, generally occur crystallized in a more or less distinct form. A current of low intensity, so long as it is capable of effecting the decomposition, is the condition favourable to the development of distinct crystals. On the contrary, a metal may be precipitated in the state of amorphous [illegible]owder by a current of great intensity. The metal will appear at the [illegible]e at which hydrogen would be evolved on the electrolytic decom[illegible]ion of water.

[illegible]RIETIES OF FRACTURE.—Except when otherwise stated, the frac[illegible] surface is supposed to be that produced in the metals at the [illegible]nary temperature of the atmosphere.

[illegible]rystalline.—Characteristic examples of this fracture are presented [illegible] zinc, antimony, bismuth, and the variety of pig-iron termed [illegible]geleisen by the Germans, from the fact of its fractured surface pre[illegible]ting large, bright, mirror-like crystalline faces.

Granular.—Grey forge pig-iron affords an instance of this kind of [illegible]cture, which may be divided into *coarse* or *fine* according to degree.

Fibrous.—When an ordinary bar of iron is broken while cold by [illegible]nding it backwards and forwards—or, in the case of a thick bar, by [illegible]tting a nick across one surface, and then bending it so that rupture [illegible]y take place along the line of the nick,—the fractured surface pre[illegible]nts a fibrous appearance. Much stress is laid upon the "fibre" of [illegible]n *thus manifested on fracture; and according to the character of the fibre a judgment is formed as to the quality of the iron.*

[illegible]inely fibrous or silky.—When a small piece of tough copper is broken [illegible]nicking it slightly on one side, and then bending it backwards and [illegible]wards until it breaks, the fractured surface will appear finely [illegible]rous and present a silky lustre. The fibre in this case seems to be [illegible]tirely produced by the repeated bending which is necessary to cause [illegible]pture; for when a large bar or ingot of tough copper is broken in [illegible]e usual manner by nicking it sufficiently across one surface, sup[illegible]rting it at its ends with the nick downwards and then striking it

with a sledge-hammer on the part opposite the nick, the fractured surface is granular and not fibrous. But in the case of bar-iron it may be shown that a fibrous structure pre-exists, and, therefore, that the fibrous appearance of its fractured surface can only be partially due to the process of bending backwards and forwards. When a bar of wrought-iron is exposed during a sufficient length of time to the action of dilute sulphuric or hydrochloric acid, it will be, as it were, dissected, and will then present the appearance of being composed of a bundle of parallel fibres; but if the bar is melted and the melted metal similarly acted upon, a *crystalline* and *not a fibrous* appearance will be produced.

Columnar.—When some of the malleable metals are heated to a certain degree and then struck with a hammer or allowed to fall on the ground from a sufficient height, they easily break into columnar pieces. The peculiar form of the grain-tin of commerce is produced in this manner.

Conchoidal.—The fracture of certain very brittle alloys is distinctly conchoidal and glass-like. An alloy consisting of 2 parts of zinc and 1 of copper furnishes a good illustration of this fracture.

MALLEABILITY: *the property of permanently extending in all directions, without rupture by pressure (as in rolling), or by impact (as in hammering).*—It is opposed to brittleness, which is the property of more or l readily breaking under compression, whether gradual or sudden; and copper are malleable, antimony and bismuth brittle.

Malleability may be much affected by temperature: thus ord copper is malleable when cold as well as when heated below a c degree; but beyond that degree it becomes so brittle, that it ma readily reduced to powder. Zinc in ingot is only malleable at a 150° C. Iron continues malleable even when near its point of fusi

Malleability is also affected by molecular condition. A metal r lose its malleability by being hammered or rolled, and can only reg it by being heated to a certain point. The method of restoring m leability by means of heat is constantly employed in the arts, and termed *annealing*. In rolling a metal—that is, in subjecting it to pr sure between strong revolving metallic cylinders, technically term "rolls," of which the axes are parallel, horizontal, and in the sa vertical plane—annealing from time to time is necessary; otherwi not only would the process proceed with difficulty, but the me would crack, especially at the edges. With some metals, for exam copper, it is immaterial whether the cooling after annealing takes p slowly or rapidly; but with others it is very material: thus, a cer alloy of copper and tin is rendered most malleable by rapid cool while steel can only be rendered malleable by slow cooling. malleability of a metal may be affected by the character of its crys line structure. Thus, when once the crystalline structure of an in of zinc is, as it were, broken down by the process of rolling at t proper temperature, the sheet of metal obtained may be much furth reduced in thickness by rolling it while cold. The hardness whi

it may thereby acquire may be removed by annealing at a low temperature; but if the sheet is heated to a degree bordering on its point of fusion, it becomes extremely brittle, whether the subsequent cooling takes place slowly or rapidly. The sheet before having been heated to this point emits no sensible crackling sound by being bent backwards and forwards; but, after having been thus heated, it emits a very audible crackling sound, due, probably, to the disruption of the crystals, which have been reproduced, by the exposure of the metal to a temperature even below its point of fusion.

Some alloys or mixtures of metals with each other undergo molecular changes in process of time, which affect their malleability. Brass wire will occasionally become very brittle, especially when kept in a state of tension. An alloy of tin and lead, which is used in pattern-casting for brass-foundry work, and which at first is comparatively hard, becomes after a time so soft as to be no longer fit for use.

DUCTILITY: *the property of permanently extending by traction, as in wire-drawing.*—Although all ductile metals are necessarily malleable, yet they are *not necessarily ductile in the exact ratio of their malleability.* Thus, iron is very ductile, and may be drawn out into very fine wire; but it cannot, like some other less ductile metals, be hammered or rolled into extremely thin sheets.

The following table of metals, arranged in the order of their malleability and ductility,[9] is usually found in books; but since the recent more exact examination of many metals by Deville and others, it will have to be considerably modified. Nickel, for example, in a state of much greater purity than hitherto prepared, has been found to possess greater malleability and tenacity than was formerly believed.

Malleability.	Ductility.
1. Gold.	1. Gold.
2. Silver.	2. Silver.
3. Copper.	3. Platinum.
4. Tin.	4. Iron.
5. Platinum.	5. Nickel.
6. Lead.	6. Copper.
7. Zinc.	7. Zinc.
8. Iron.	8. Tin.
9. Nickel.	9. Lead.

TENACITY: *the property of resisting rupture by traction.*—It is proportionate to the weight which the wire of a given metal is capable of sustaining. To determine the tenacity of different metals, wires *of exactly the same diameter*, or which have passed through the same *draw-plate*, must be prepared; and the utmost weight, which each wire is capable of suspending without breaking, must be exactly determined. This weight is *the measure of the resistance to rupture*, or *the tenacity.* Tenacity is much affected by molecular condition, especi-

[9] Regnault, Cours élémentaire de Chimie, ii. 26. This table is nearly the same as that of Thénard, Tr. de Ch. 6ième éd. tom. ii. p. 12.

ally crystalline structure. The presence of foreign matters, even in very minute proportion, may affect the tenacity of a metal in a material degree. This circumstance, and that of difference of molecular condition consequent on previous treatment, mechanical or other, will explain the variations which *apparently* the same metal may present in respect to tenacity.

As might have been anticipated, variation in temperature even within comparatively narrow limits, is found to occasion considerable variation in the tenacity of metals. Baudrimont has published the following results on this subject.[1]

TENACITY OF THE PRINCIPAL MALLEABLE METALS AT THE TEMPERATURES 0°, 100°, AND 200° C., AS FOUND BY EXPERIMENT, WITH THE TENACITY CALCULATED FOR 1 SQUARE MILLIMETRE OF SECTIONAL AREA (0·0155 SQUARE INCH).

Metals.	Diameter at 16°. 1 millimetre = 0·03937 inch.	Tenacity			Tenacity calculated for 1 sq. mm. of sectional area.		
		at 0°.	at 100°.	at 200°.	at 0°.	at 100°.	at 200°.
	millimetres.	grms.	grms.	grms.	grms.	grms.	grms.
Gold	0·41250	2459	2035	1722	18400	15224	12878
Platinum	0·41000	2987	2546	2281	22625	19284	17277
Copper	0·48000	4542	3958	3296	25100	21873	18215
Silver	0·39825	3528	2898	2314	28324	23266	185[illegible]
Palladium	0·39750	4527	4031	3360	36481	32484	27[illegible]
Iron	0·17500	4940	4611	5057	205405	191725	210[illegible]

Baudrimont gives the following summary of his results:—

1. The tenacity of metals varies with the temperature.
2. It decreases generally, but not without exceptions, when t[illegible] temperature increases.
3. With silver it diminishes more rapidly than the temperature.
4. With copper, gold, platinum, and palladium, it decreases l[illegible] rapidly than the temperature.
5. Iron presents a special and very remarkable case: at 100° i[illegible] tenacity is less than at 0°, but at 200° it is greater than at 0°.

Séguin has obtained the following results: the tenacity of each meta[illegible] is assumed to be 100 at 10° C.[2]

Temperature.	Iron.	Copper.	Brass.
10°C.	100	100	100
370°	90·5	36·6	19·6
500°	58·7	..	..

TOUGHNESS.— This term, which is nearly allied to tenacity, is constantly in use amongst practical metallurgists to denote the property

[1] Ann. de Ch. et de Phys. 3. s. 30, p. 304 *et seq.* 1850.

[2] Comptes Rendus, 1855, 40. p. [illegible]

of resisting extension or fracture by tearing or bending. Thus a piece of copper is said to be tough in proportion to its capability of being bent backwards and forwards without breaking. One of the varieties of copper known in commerce is called *tough-cake*. The following illustration of the term toughness, as applied to steel, was given by Dr. Young:[3]—"Steel, whether perfectly hard or of the softest temper, resists flexure with equal force when the deviations from the natural state are small; but at a certain point, the steel, if soft, begins to undergo an alteration of form; at another point it breaks if much hardened; but when the hardness is moderate, it is capable of a much greater curvature, without either permanent alteration or fracture; and this quality, which is valuable for the purposes of springs, is called *toughness*, and is opposed to *rigidity* and *brittleness* on the one side, and to *ductility* on the other."

SOFTNESS.—This term is used to denote the property of a metallic mass of *easily* yielding to compression without fracture, and not returning to its original form after the removal of the compressing force; and in this sense it is opposed to elasticity. It is the property essentially concerned in the striking of medals. It is also used by metallurgists in the sense of being easily *sectile*. Strictly speaking, the term *soft* must always be comparative; but in metallurgical language, while [illegible]is frequently used comparatively, it has yet a more absolute mean-

Thus metals are practically divided into *soft* and *hard*; lead and [illegible]are examples of the former, copper and iron of the latter. But [illegible]eties of the same *soft* metal are constantly compared with each other [illegible]espect to softness; thus commercial varieties of lead are divided [illegible] *soft* and *hard*. The *hard* metals are also similarly compared with [illegible] other; steel is said to be *soft* or *hard* according to the condition [illegible]uced by previous special treatment.

[illegible]emperature must obviously have the greatest influence in deter-[illegible]ning the softness of a metal. At the ordinary temperature, potassium [illegible]ongst the rarer metals, and lead amongst those in common use, are [illegible]mples of the softest metals; while the *least soft*, or *hardest* metal by [illegible] is the native osmium-iridium alloy, which is much harder than the [illegible]rdest steel. Chromium is also extremely hard—indeed, sufficiently [illegible] to *cut* glass. What the *actual* effect of the *deprivation* of heat might [illegible] in determining *hardness*—whether, for example, lead would at any [illegible]gree of reduction of temperature become as hard as iron—we have [illegible] means of knowing. But we do know positively the effect of the [illegible]lition of heat in determining softness.

CONDUCTION OF HEAT AND ELECTRICITY.—One of the most prominent [illegible]aracters of the metals is, certainly, their superior power of con-[illegible]cting heat and electricity. The following results on the conductivity [illegible] metals for heat, which have been obtained by Wiedemann and

[3] Nat. Phil. i. 142.

Franz,[4] are stated numerically in the following table, the conductivity of silver being assumed to be 100 :—

	At 12° C.		At 12° C.
Silver	100	Steel	11·6
Copper	73·6	Lead	8·5
Gold	53·2	Platinum	8·4
Brass	23·6	German silver	6·3
Brass (thick)	24·1	Rose's fusible metal	2·8
Tin	14·5	Bismuth	1·8
Iron	11·9		

So long ago as 1833,[5] Professor J. D. Forbes of Edinburgh was led to infer that "the order of conducting power of the metals for *heat* and for *electricity* is the same;" and that this inference is very probably correct will appear from the following table of the conductivity of various metals for electricity :—

	Riess.	Lenz.	Arndtsen.[6]	Matthiessen.[7]	
				Hard-drawn.	Annealed.
	At 15° C.	At 0° C.	At 0° C.		
Silver	100	100	100*	At 0° C. 100*	110
Copper	66·7	73·3	98·7	,, 99·5*	102
Gold	59 0	58·5	...	,, 78*	80
Brass	18·4	21·5	25·4	.. ..	..
Tin	10·0	22·6	...	At 21° C. 11·4*	..
Iron	12·0	13·0	14·8	.. ..	..
Steel	...	...	...	At 20°4 C. 14·4	..
Lead	7·0	10·7	9·1	At 17°3 C. 7·8*	..
Platinum	10·5	10·3	14·5	At 20°7 C. 10·5	..
German silver	5 9	...	18·7	At 18°7 C. 7·7	..
Bismuth	...	1·9	...	At 13°8 C. 1·2*	..

Those marked * are stated by the authors to have been pure.

Whatever the quality may be upon which calorific conduct depends, it is, as Professor Tyndall remarks, "exceedingly proba that the same quality influences in a similar manner the transmiss of electricity; for the divergences of the numbers expressing conductivity for heat from those expressing the conductivity electricity, are not greater than the divergences of the latter alo exhibited by the results of the different observers."

In the case of iron, Professor Forbes states that he has found t conductivity for heat to vary with the temperature; or, in his o words, that "the flux of heat through the solid is not in a sim direct proportion to the difference of temperature of two contigu thin slices, but varies in a less rapid proportion; or, the conductiv diminishes as the temperature increases."[8] When the statement w announced, he had only experimented upon iron.

[4] Poggendorff's Ann. b. 89, p. 497. An account of these researches has been given by Professor Tyndall in the Philosophical Magazine (vol. vii. p. 33, 1854.)

[5] Phil. Mag. vol. iv. p. 27, 1834.

[6] Poggend. Ann. b. 104, p. 1.

[7] Phil. Trans. 1858.

[8] Brit. Ass. Rep. 1852, p. 261.

The conductivity of metals for electricity has been found to vary with the temperature. The following experiments on this subject have been made by Lenz[9] and Arndtsen: the conductivity of each metal is estimated as 100, at 0°C.

	Lenz.			Arndtsen.	
	At 0°C.	At 100°C.	At 200°C.	At 100°C.	At 200°C.
Silver	100	74·5	56·6*	74·5	59·4*
Copper	100	77·7	61·0	73·0	57·5
Gold	100	84·9	73·7	..	..
Tin	100	71·8	53·4	..	..
Brass	100	87·6	78·0	87·3	79·9
Iron	100	67·7	46·2	67·2	49·1
Lead	100	71·4	52·3	72·6	57·0
Platinum	100	81·0	68·0	75·3	60·4

Mr. Matthiessen, to whom I am indebted for his assistance in the preparation of the foregoing tables, finds that the electric conductivity of many metals is affected in a remarkable degree by certain foreign matters, when present even in very small proportion.

It is probable that the conductivity of all metals for heat and electricity will be affected by molecular condition; for, according to Berzelius,[1] copper wire conducts electricity better after having been heated to redness, and soft steel better than that which has been hardened; and similar results by Matthiessen are given in the last table but one. The molecular condition of metals is, as has been stated, changed, not only by various mechanical processes, but especially by the rate of cooling after fusion or exposure to heat. Hence, in researches on the conductivity of metals, it is important to note not only the degree of purity and temperature of the specimens operated upon, but also the precise treatment which they may have received; for, otherwise, satisfactory comparisons cannot be made between the results of different observers. It seems most probable that the conductivity of metals may be modified by the presence of foreign matter, even in minute proportion, which, it is well known, may frequently induce a sensible alteration in the mechanical properties of metals. It is not unlikely that the investigation of the subject may yield important practical results. If, for example, it should be found that specific degrees of conductivity for heat of different kinds of iron should correspond to specific qualities in the steel produced from such kinds of iron respectively, the manufacturer of steel might apply the information with considerable advantage.

CAPACITY FOR HEAT.—Equal weights of different metals require different amounts of heat to raise them from the same to a higher given temperature. The amount of heat necessary to raise 1 part by weight

[9] Mém. de l'Acad. Imp. des Scien. de St. Pétersbourg, sér. 6, t. 1, p. 439, 1838.

[1] Berzelius, Traité de Chimie, t. 2, p. 6, Paris, 1846.

of water from 0° C. to 1° C. being 1, the amounts of heat required respectively to raise the same weight of the following metals from 0° C. to 1° C. will be as follow:[2]—

Iron	0·1138	Cadmium	0·0567
Nickel	0·1086	Tin	0·0562
Cobalt	0·1070	Antimony	0·0508
Zinc	0·0955	Platinum	0·0324
Copper	0·0952	Gold	0·0324
Palladium	0·0593	Lead	0·0314
Silver	0·0570	Bismuth	0·0308

EXPANSION BY HEAT.—Metals expand when heated, and within certain limits generally in a degree proportionate to the temperature. This subject is of great practical importance. The degree of expansion for each metal will be stated in due course in this work.

OPACITY, *or the property of intercepting the passage of light.*—All metals, whether in the liquid or solid state, may be regarded as perfectly opaque, except in certain cases of extreme thinness. Thus a greenish light traverses gold-leaf. As the light which is thus transmitted is polarized, it is certain that it passes through the substance of the metal, and not through minute holes, which might be supposed to be produced in the process of gold-beating. Silver-leaf, on the con trary, is perfectly opaque. But the light which traverses leaf p pared from gold alloyed with a certain proportion of silver is purp instead of greenish.[3]

LUSTRE.—The characteristic lustre, termed *metallic*, is due to manner in which light is reflected from the polished surfaces metals. It is variable with the nature of the metal and the degr polish. Metals in a state of fine division, like copper precipitated solution by iron, do not present their characteristic lustre, but im diately acquire it when the powder is rubbed with a burnisher.

COLOUR.—It is difficult to frame any classification of the met founded upon colour which shall in all respects be quite satisfacto but the following may probably be adopted as at least convenient a practical:[4]—

White.—a. *Silver-white.*—Silver must be classed alone in this divisio

b. *White, inclining to silver-white.*—Tin, cadmium, or mercur may be taken as examples.

c. *White, inclining to blue.*—Antimony, zinc, lead.

d. *Yellowish-white.*—Bismuth.

Grey.—The varieties of pig-iron, known as *grey-pig*, furnish cha racteristic examples of this colour.

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[2] Regnault, Cours élémentaire, t. 2, p. 28.

[3] This subject of the transmission of light through gold in a state of fine division has been investigated by Faraday, whose results are recorded in th Philosophical Transactions, 1857.

[4] Vide Thénard, Tr. de Ch. 6ième éd t. 2, p. 8.

Yellow.—Gold, certain alloys of copper and zinc, and copper and tin.

Red.—Copper, which varies in colour from purplish-red to orange. The peculiar copper-coloured compound of titanium, which is found in the hearths of blast-furnaces in this country, and which at one time was mistaken for copper, is the only other metallic substance which has the colour and lustre of copper.

Violet.—The alloy of copper and antimony, which the alchemists called the *regulus of Venus*, has a characteristic and beautiful violet colour.

GENERAL CONSIDERATIONS ON METALLURGICAL PROCESSES.

ORES.—The term ore is applied to the metalliferous matter in the [illegible]n which it is extracted from the earth by the miner.

[illegible]als occur in the earth either in the metallic state or in the state [illegible]mical combination as sulphides, oxides, and carbonates, or, more [illegible]y, as arsenides, chlorides, sulphates, phosphates, and silicates. [illegible] term *native* is used to express their occurrence in the metallic [illegible]e: thus gold and platinum occur native. Native metals are not [illegible]essarily pure: thus no instance is recorded of native gold free [illegible]m silver.

Ores exist in the earth either in veins or beds. Veins have been [illegible]med by the filling up of cracks or fissures in rocks, with metalli[illegible]ous and non-metalliferous matter, or matter, rather, which contains [illegible] metal the object of extraction by the miner. Such matter is [illegible]med *vein-stuff*, *matrix*, or *gangue*. Sometimes a vein is found enlarged [illegible]o cavities of considerable size filled with ore. When the vein is [illegible]arrow, the rock forming its walls or cheeks must be excavated to a [illegible]ertain extent, and in this case the ore may, in addition to the vein [illegible]tuff proper, contain more or less of the rock which the vein traverses. [illegible]res from beds may be mixed with the substance of the roof or floor of [illegible]e mine, or, in the case of nodules arranged in beds, with the substance in which they are imbedded. It may be convenient, for the sake of brevity, to designate as *extraneous* matter everything in the ore except the metallic *mineral species* which is the object of search by the miner.

This extraneous matter is separated in a greater or less degree by the mechanical processes of *dressing* practised at the mines; but in some cases it would not be expedient, even were it practicable, to effect the complete separation of this matter, which may serve an important purpose in the metallurgical treatment of the ore. Thus, in the extraction of copper from copper-pyrites silica is essential for the

removal of the iron. The extraneous matter generally consists of one or more of the following substances:—silica, in the form of quartz; various silicates, such as felspar and mica in granite, hornblende, clay-slate, &c.; carbonate of lime, carbonate of magnesia, sulphate of baryta, and fluorspar.

METALLURGICAL PROCESSES.

They may be divided into *dry* and *wet*, according as they are conducted without or with the agency of liquid reagents. The terms *pyro-* and *hydro-metallurgical* have been proposed instead of dry and wet, but they possess no advantage over these short, explicit, and generally accepted words. In some instances a metal is extracted by a combination of dry and wet processes. It is not always that a metal is required to be separated from its ore in the *metallic* state.

CLASSIFICATION OF PROCESSES.—The various kinds of metallurgical processes may be classified as follows:—

1. Separation of the metal without fusion of the ore.
   - *a.* Direct without reduction.
   - *b.* Indirect with reduction.
2. Separation of the metal with fusion of the ore.
   - *a.* Simple fusion.
   - *b.* Simple reduction with fusion.
   - *c.* Reduction with volatilization of the metal.
   - *d.* Reduction by complex processes with fusion.

REDUCTION.—When a metal is separated from a state of *chemical* combination, it is said to be *reduced*, and the process of separation is term *reduction*. The agent, by which the reduction is effected, is term *reducing-agent*. Thus, when charcoal is heated with oxide of lead, c bonic acid is formed and the lead is reduced to the metallic state; when iron is heated with sulphide of lead, sulphide of iron is form and the lead is also reduced to the metallic state. In these cases th carbon and iron are reducing agents. The term reduction is also use to express the *partial* separation of the electro-negative element of metallic compound. Thus, it is usual to speak of the reduction of oxide from a *higher* to a *lower* degree of oxidation. The metals whi may be reduced from their combinations with oxygen by the action of heat alone were formerly termed *noble*, whereas the metals of which the oxides cannot be so reduced were termed *base*. When the oxides and sulphides of certain metals are heated together complete reduction takes place, and in such cases the oxides and sulphides may equally be regarded as reducing-agents. It is not correct to apply the term reduction to the simple separation of a metal which exists in the *metallic* state in its ore.

Reduction by carbon.—When an oxide is *easily* reducible, like oxide of lead, carbonic acid will always be formed, whatever may be the pro

portion of carbon. The carbon is converted directly into carbonic acid, just as when it is burned in oxygen or atmospheric air; and the temperature at which the oxide is reduced is not sufficient to cause the reduction of the carbonic acid to carbonic oxide by the carbon present, a comparatively high temperature being required to produce that effect. When the oxide is *not easily* reducible—such as oxide of zinc—carbonic oxide will always be formed, because the temperature required for its reduction is so high, that, supposing carbonic acid in the first instance to be formed by one portion of the carbon, it would be immediately reduced to carbonic oxide by another portion of the carbon before any further reduction of the oxide could be effected. It must be borne in mind that in any merely mechanical mixtures the oxide and carbon must exist in comparatively large particles. In these processes of reduction it is necessary to consider the action of *quantity*: thus carbonic oxide reduces oxide of zinc at a high temperature, with the formation of an equivalent proportion of carbonic acid; and zinc reduces carbonic acid to carbonic oxide with the formation of an equivalent proportion of oxide of zinc. The case is exactly analogous to the decomposition of water at a high temperature by iron and the reduction of oxide of iron by hydrogen. Hence there should be a mixture of carbonic acid and carbonic oxide, to which zinc might be exposed at a given temperature without ge; or a mixture of hydrogen and steam to which iron might be ed without change. Debray has investigated this subject, and l the following results.[5] When mixtures of hydrogen and e passed over heated sesquioxide of iron in the proportions of , H^2+HO, H^3+HO, black protoxide of iron is always formed, which the magnet has no action, which easily burns with the tion of magnetic oxide, and dissolves in hydrochloric acid t the evolution of gas. In the proportion of H^4+HO sesquioxide n is reduced to the metallic state. When hydrogen and steam assed over the reduced iron in the proportions of H^8+HO, O; $H+HO$, there is *perfect equilibrium*. When a mixture of carcid and carbonic oxide, in the proportion of CO^2+CO, is passed squioxide of iron, it is reduced to the state of protoxide. This re is without action on metallic iron, but it reduces the oxides el, cobalt, and zinc, to the metallic state.

as maintained by Le Play[6] that *solid* carbon could not directly he reduction of metallic oxides. His conclusion was founded following considerations:—1. He remarked with astonishment zinc-works it was regarded as a matter of indifference whether e and carbonaceous reducing-agent were intimately mixed or The ore consists essentially of oxide of zinc, from which the

mptes Rendus, 1857. 45, p. 1018.

he following observations are abed from the excellent paper of ussac, entitled 'Remarques sur la e de M. Le Play, ingénieur des Mines, touchant la réduction des oxydes métalliques par le charbon.' Annales de Chim. et de Phys., 3, s. 17, p. 221. 1846. I have adhered as far as practicable to the language of Gay-Lussac.

metal is always reduced by carbonaceous matter. Le Play then inferred that *carbonic oxide alone* was the reducing-agent. 2. He ascertained, during numerous metallurgical travels, that in all blast-furnaces in which the oxides of iron, lead, copper, and tin are reduced, there is no appreciable contact between the ores and the charcoal; that the operation does not even succeed when the mixture is as complete as possible; and that, on the contrary, the more insignificant the contact the better will be the working of the furnace. 3. Le Play and Laurent reduced various oxides and salts by heating them in a porcelain tube through which passed a current of carbonic oxide. Thus hæmatite and a crystal of specular iron ore were perfectly reduced by this means; so also were the oxides of cobalt, nickel, and tin. Tungstic acid was likewise reduced to the metallic state, but the oxides of cerium, chromium, and titanium suffered no change. Crystals of sulphate of baryta and sulphate of lime were converted into sulphides. 4. They heated in a porcelain tube a crystal of sesquioxide of iron and a piece of charcoal, each being contained in a separate platinum trough in order to prevent contact, and the oxide was perfectly reduced to the metallic state.

In all these cases it is very easy to conceive, as Gay-Lussac remarks, that reduction may be effected by carbonic oxide when it is capable of reducing the oxide of the metal. This gas, forming an atmosphere around the pieces of ore and penetrating into the sma interstices, ought to effect a more rapid reduction than charcoal which the contact must be less intimate. Let a piece of charco mass of metallic oxide be kept separate and heated in a confin from which gas may escape; they will react upon each other, j the space were originally filled with carbonic oxide, carbonic a even atmospheric air, and provided the temperature be suffic convert carbonic acid into carbonic oxide at the moment of c with charcoal. Carbonic oxide reduces the metallic oxide wi formation of carbonic acid; this carbonic acid is converted bac carbonic oxide by contact with charcoal at a high temperature, the action is propagated continuously, carbonic oxide being the by which the oxygen of the oxide and the solid carbon are con

Now, because reduction may be effected under the conditions by the agency of carbonic oxide, it by no means follows tha carbon is incapable of reducing oxides by direct contact. contrary, Gay-Lussac states that, when strongly calcined lam is heated with easily-reducible oxides—such as oxides of silv cury, copper, lead, bismuth, &c.—reduction takes place belo heat, and much below the temperature at which carbon ca vert carbonic acid into carbonic oxide, only absolutely pure ca acid being evolved. With all these oxides reduction is di effected by carbon, and cannot be attributed to carbonic oxide, is not present. No doubt, he continues, carbonic oxide woul fectly well reduce these oxides at a suitable temperature, an suredly, more rapidly than carbon; but that is not the question is sufficient to demonstrate that carbon alone, at a very mod

degree of heat, reduces metallic oxides without the intervention of carbonic oxide or any other elastic fluid.

The temperature at which oxide of silver may be reduced by solid carbonaceous matter has been investigated in my laboratory by Mr. A. Dick. Oxide of silver was prepared by precipitation with potash from nitrate of silver. Intimate mixtures were made of 116 grains of the oxide with 6 of wood-charcoal—116 of oxide and 6 of carbon obtained from the imperfect combustion of coal-gas—and 116 of oxide with 3 of the same carbon. These mixtures were heated in the hot-air bath. The first exploded quietly at 262° C., and another similar mixture at 270° C.; the second exploded rather violently at 178° C.; the third exploded at 185° C.; and in two repetitions of the experiment with this mixture the explosion occurred at 172° C. and 178° C. respectively. In all the experiments the metal remained in the state of fused globules. No oxygen was evolved from the oxide heated *per se* at these temperatures. Perhaps an objection might be raised against the conclusiveness of these experiments on the ground that the carbon employed was not free from hydrogen.

"But, independently of oxides," continues Gay-Lussac, "which carbon directly reduces at a temperature below that at which it decomposes carbonic acid, there are many others which resist carbonic oxide, even at a very high temperature, and are yet reducible by carbon. Such are the oxides of manganese, chromium, cerium, titanium, potassium, &c."

Since, then, carbon directly reduces oxides which require only a rate heat and those which require a very high heat—conditions ich carbonic oxide produces no effect—is it not evident that it reduce oxides at an intermediate degree of heat when carbonic is able to effect reduction at that temperature? But in stating carbon would then act concurrently with carbonic oxide in the tion of oxides, we only wish to establish the fact, as we are ver convinced that in consequence of the contact of that gas he ore being much more intimate than can possibly be the ith carbon, it ought to effect reduction with much greater y."

Play was misled by seeing the reduction of oxides apparently d on a very large scale in metallurgical works by the sole y of carbonic oxide, and he erroneously inferred that the action bon was nothing because it seemed to him insignificant. The nce in the action of these two bodies whenever they are in the ice of an oxide which each has the power of reducing is, without t, very great, but it is not the less due to purely mechanical s, and the action of the one body ought not to be ignored, because, rticular cases, it may be much inferior to that of the other."

hen a piece of hæmatite, even of large size, is kept exposed to the n of carbonic oxide at a high temperature during a sufficient time, ay be completely reduced to the metallic state, even to the very re, and yet metallic iron at the same temperature will reduce carbic acid. Supposing the reducing action of carbonic oxide to be

equal in power to the oxidizing action of carbonic acid, then no action should take place when a molecule of oxide of iron, or one of metallic iron, is heated in the presence of a mixture of one molecule of carbonic oxide with one of carbonic acid. "If we now conceive," says Gay-Lussac, "a molecular pore to have become free by the abstraction of a molecule of oxygen which filled it, and a molecule of carbonic oxide to have been introduced instead, there will be no reason why it should act on a neighbouring molecule of oxide; for, if the reduction were possible, a molecule of iron and a molecule of carbonic acid would be in the presence of each other, and should just as well, by their reciprocal action, reproduce oxide of iron and carbonic oxide. In order that, according to the present supposition, reduction might occur, several molecules of carbonic oxide should find their way into the molecular pore, which may well be conceived to be impossible. Hence, in the present example, and many others of a similar kind, carbonic oxide cannot penetrate into the interior of masses and effect reduction. And yet there is no doubt that it is the chief agent in the reduction of iron ores, because it finds, not molecular pores, but innumerable fissures in the ore, which facilitate its access in mass towards each molecule. This example manifests the inefficacy of carbonic oxide, even in circumstances in which its power suffices for reduction, and that its action is not so simple, so heroic, or so general as MM. Le Play and Laurent have thought."

SMELTING.—The term is derived from the German verb *schmelzen*, to melt. It is applied to a process, or series of processes, by which a metal or metallic compound is separated by fusion from its ore on a large scale.

Flux and slag.—The following illustration will serve to explain the meaning of these terms, which are in constant use. In auriferous quartz the gold exists in the metallic state, and is diffused throughout the mass in particles. When such quartz, either in lumps or in the form of the finest powder, is heated to a degree far above the melting point of gold, perfect separation of the metal cannot occur, because the melted particles are surrounded by solid quartz, and cannot therefore subside and unite. If the gold were present in large quantity, it is true that, by stirring, it might be imperfectly collected together; but by the addition of carbonate of soda a fusible silicate of soda would be formed, and the melted gold, having a much higher specific gravity than silicate of soda, would immediately sink and collect into one mass at the bottom. The carbonate of soda in this case would be designated a *flux*, and the resulting silicate of soda a *slag*. Other matters, such as oxide of iron, lime, and clay, &c., would act in a similar manner to carbonate of soda, that is, they would form fusible compounds or slags with the quartz and so allow the gold to settle down.

The nature of the flux must obviously vary with the nature of the extraneous matter in the ore. In the case of auriferous quartz it is essential that the quartz should be wholly and completely fu[illegible]

otherwise a sensible amount of gold might remain imprisoned in any unfused pieces. However, it is not necessary that in every smelting operation the fusion of extraneous matter should be so completely effected. In one process in particular we shall find that pieces of quartz as large as nuts remain diffused through a slag, producing a pseudo-porphyritic appearance. The slag in which they are imbedded having itself been well melted, the metallic matter, in consequence of its exceeding in specific gravity both the slag and the quartz, has been enabled to subside.

Regulus.—In the smelting of certain sulphuretted ores the product obtained in the first instance is a *sulphide* of the metal; and this product has received different names in different metallurgical works. In English copper-works the word *metal* is commonly used to denote compounds of this kind: that of *regulus* being applied in a specific sense to certain kinds of *metal*. I shall, however, adopt the word *regulus* in the present work as a generic appellation for all similar products. The Germans designate regulus by the synonymous terms *Stein* and *Lech*, and the French by the term *matte*. It is frequently the case that in one smelting operation *slag*, *regulus*, and *metal* are obtained, which are superposed in the order mentioned, which is that of their respective specific gravities.

Speise.—In the smelting of arsenical ores the product obtained in the first instance is an *arsenide* of the metal, which the Germans call *Speise*, a convenient word now in general use. In one smelting operation may be obtained *slag*, *regulus*, *speise*, and *metal*.

ROASTING.—This term, with which *calcination* is occasionally used nonymous, is applied to processes which in nature and ob- may differ much from each other. The object of roasting may erely the expulsion of certain volatile matters from ores or other nces, by the simple effect of heat, or by the conjoint effect of nd air, when oxidation will occur; or the object may be only to oxidation. Roasting may be conducted in the open air by the ore mixed with fuel in large heaps, or in flat-bedded rever- y furnaces. Numerous illustrations of both methods will d in the sequel. A reverberatory furnace consists essentially e parts—a fireplace at one end, a stack or chimney at the and a bed between both, on which the matter is heated. The ce is separated from the bed by a low partition-wall, called the idge, and both are covered by an arched roof, which rises the end wall of the fireplace and gradually dips toward the fur- end of the bed connected with the stack. On one or both sides e bed, or at the end near the stack, may be openings through h the ore spread over the surface of the bed may be stirred about exposed to the action of the air. The matter is heated in such rnace by flame, and is kept from contact with the solid fuel. The e in its course from the fireplace to the stack is reflected down- ds or *reverberated* on the matter beneath, whence the name *reverbe- ry* furnace.

In roasting in reverberatory furnaces, the object is generally the expulsion of certain volatile matters, and the oxidation, more or less complete, of the residue. The matter should be spread uniformly over the bed, and stirred or raked about from time to time, in order freely to expose every part in succession to the action of the air. The heat should be gradually raised; and in the case of ores which readily melt, care must be taken at first to prevent clotting, by suitably regulating the heat and stirring frequently. When sulphuretted or arsenical ores are roasted until no further evolution of sulphurous acid or arsenious acid takes place, the roasting is termed *sweet* or *dead*. In some cases *sweet* roasting is necessary, in others not; but when necessary, the ore should be reduced to fine powder. The rapidity of roasting will depend upon the state of division of the matter, upon the temperature, and upon the frequency with which the action of the air is promoted by stirring. When an ore is allowed to *clot* during roasting, the process will obviously be much retarded.

Distillation.—In the metallurgical treatment of the ores of certain volatile metals, the metal is volatilized and its vapour condensed. When the vapour passes from the bottom of the vessel containing the ore, the process is called distillation *per descensum;* but when the vapour passes out at or near the top, the process is called distillation *per ascensum*. ..

Sublimation.—This term is applied to the volatilization of a metal or metallic compound by heat, and its condensation in a solid form.

Liquation.—When an ore or metallic mixture containing ingred differing sensibly in fusibility, is exposed to a degree of heat suffi only to melt the most fusible, which may flow away from the unm mass, the process is termed liquation.

SLAGS.

Silica plays a very important part in numerous metallurgic rations in the formation of slags, which, excepting those pr in processes of assaying, and, in a few instances, on the large sca always silicates.

Silicates may be divided into anhydrous and hydrated sil thus, augite and felspar are examples of the former, and a zeoli porcelain clay are examples of the latter. All silicates produ metallurgical processes by the action of heat are anhydrous, th not necessarily so, as Bunsen has shown that a hydrated silica lime may be prepared at a red heat. When a finely-pounded mix consisting of 0·2 of lime and 1·0 of silica by weight, is introd into 9·0 of caustic potash melted in a silver capsule, and the w allowed to cool slowly, after having been kept for some time strong (?) red heat in a muffle, a mass is obtained, which, w treated with water, leaves a network of prismatic crystals, freque

4 or 5 lines in length, partly attached to the sides of the capsule. These crystals are hydrated silicate of lime mixed with some carbonate of lime, and their composition is expressed by the formula—

$$3\,CaO,\,2\,SiO^3 + Aq.$$

They were found on analysis to consist of—

Silica	27·215
Lime	22·241
Potash	0·733
Water separated at 228·2 F.	36·915
Water separated by ignition	9·508
Carbonate of Lime	2·603
	99·215

This hydrated silicate of lime loses the whole of its water below a red heat after the potash, in which it was formed, has been dissolved out.[7] It is scarcely necessary to call attention to the fact that water cannot be separated by heat from hydrated oxide of potassium or potash.

Silicates are either crystallized or amorphous: felspar is an example of the former, and porcelain-clay an example of the latter.

The bases which most frequently occur in slags are lime, magnesia, protoxide of manganese, protoxide of iron, potash in small quantity, and alumina. Both the silica and the bases are derived from the extraneous matter in the ore, the ashes of the fuel, the flux added, and, in a certain degree, from the materials of which furnaces are constructed. Silicates, of which the constituents are derived from these sources, may be produced in smelting the ores of any metal; and such silicates only will be considered in this place: silicates which are formed in special metallurgical processes will be described in due course. The extraneous matter of an ore may be fusible *per se*, in which case no flux would be necessary. It is only in blast-furnaces that the ashes of the fuel enter into the composition of the resulting slag.

Atomic constitution. — The old formula of silica, SiO^3, will be adopted in this work. Our knowledge of the *rational* constitution of silicates, which contain bases both of the RO and R^2O^3 types, is far from satisfactory. Thus alumina, which belongs to the latter type, [illegible]inly in many cases acts the part of the electro-negative element, or [illegible] in the spinels, for example. It has, however, been the custom [illegible]d alumina as an electro-positive element in silicates in which [illegible]pes of bases are present; but whether this view is in all cases [illegible] seems doubtful. However, there can be no doubt that alumina [illegible]t the part of base in compounds from which the RO type is absent, [illegible]orcelain-clay, for example. The nomenclature used by different [illegible]s in respect to silicates is not uniform. Thus, a silicate in which [illegible]ygen of the base is to that of the acid as 1 : 3 is termed a *neutral* [illegible] by some and a *tri-silicate* by others.[8] In this work a silicate will

[illegible]ientific Memoirs, 1853, p. 67.

[illegible]heerer, Lehrbuch d. Metallurgie, 32; Rammelsberg, Lehrb. d. Chemisch. Metallurgie, 30.

be regarded as neutral when the oxygen of the silica is to that of the base as 3 : 1; when it is as 3 : 2 the silicate will be termed bi-basic, and so forth. Various relations may occur in silicates between the base and the acid, as, for example, the following:—

Silicate containing a base of the RO type.	
1. $3RO, SiO^3$	Tribasic silicate.
2. $2RO, SiO^3$	Bibasic silicate.
3. $3RO, 2SiO^3$	Sesquibasic silicate.
4. RO, SiO^3	Neutral silicate.
5. $RO, 2SiO^3$	Bisilicate.
6. $RO, 3SiO^3$	Tersilicate.

As at present no uniform system of nomenclature has been adopted in respect to silicates, confusion is apt to arise from the different terms which are used to express the same formulæ; and this confusion is increased by the want of agreement amongst authors as to the equivalent of silica, some retaining the original formula of Berzelius, SiO^3, and others employing the modern formula, SiO^2. Moreover, metallurgical writers frequently use a particular method of notation to express the composition of the silicates of common occurrence. Single letters are used as symbols to represent both bases and silica. Thus, C, M, A, S, express lime, magnesia, alumina, and silica, respectively. The relation between the oxygen of the base and the acid is indicated by small index letters placed on the right and near the top of each symbol, except when unity is intended, and then the index is omitted. By this method the formula $3CaO, 2SiO^3$ would be expressed by the symbols CS^2; that of $3MgO, SiO^3$ by the symbols MS; and that of $Al^2O^3, 2SiO^3$ by the symbols AS^2. In the following table are presented illustrations of this method of notation and of variations in nomenclature. The numbers in the first column correspond to those of the first column in the preceding table.

1. RS	Mono or singulo silicate.
2. R^2S^3	Two-thirds or sesqui-silicate.
3. RS^2	Bisilicate.
4. RS^3	Trisilicate.
5. RS^6	Hexsilicate.
6. RS^9	Nonosilicate.[9]

If the formula SiO^2 be adopted, then the following formulæ w[illegible] respond to the terms which occur in the first table, RO, SiO^2 b[illegible] garded as a neutral silicate.

1. $2RO, SiO^2$	Tribasic silicate.
2. $4RO, SiO^2$	Bibasic silicate.
3. $3RO, SiO^2$	Sesquibasic silicate.
4. $2RO, 3SiO^2$	Neutral silicate.
5. RO, SiO^2	Bisilicate.
6. $2RO, 3SiO^2$	Tersilicate.

[9] It is much to be regretted that Greek and Latin numerical prefixes should not be applied with more discrimination at present.

The formulæ which correspond to the *formulæ*,—*not the terms*,—in the first table are as follow:—

1. $2RO, SiO^2$.	4. $2RO, 3SiO^2$.
2. $4RO, 3SiO^2$.	5. $RO, 3SiO^2$.
3. RO, SiO^2.	6. $2RO, 9SiO^2$.

Constitution.—It may be definite or indefinite. If indefinite, the slag must consist of a mixture of two or more definite silicates,—or of a mixture of one or more definite silicates with matter mechanically diffused,—or in some cases, perhaps, of a solution of one silicate in another. Slags may occur distinctly crystallized, and yet not have a perfectly definite constitution, owing to the presence of enclosed foreign matter, which can in no way enter into their formulæ. The same fact is exemplified in many well crystallized natural minerals. A slag which occurs crystallized in perfectly-defined and translucent square prisms, and which is produced in the blast-furnaces of South Staffordshire, may serve as an illustration. The following is one of several analyses of this kind of slag made by myself many years ago:[1]—

			Oxygen.
Silica	38·05		19·76
Alumina	14·11		6·59
Lime	35·70	10·03	13·35
Magnesia	7·61	2·94	
Protoxide of manganese	0·40	0·09	
Protoxide of iron	1·27	0·29	
Potash	1·85		0·31
Sulphide of calcium	0·82		
	99·81		

The oxygen of the silica is very nearly equal to that of the bases, but the oxygen of the lime (RO) bases is rather more than double that of the alumina (R^2O^3). The constitution of this slag may be expressed by the formula

$$R^2O^3, SiO^3 + 2\,(3RO, SiO^3).$$

It is the same as the formula assigned by Damour to the natural mineral Humboldtilite. The sulphide of calcium—it is inferred, but not proved, that the sulphur exists in this state of combination—cannot be regarded as in any way connected with the formula. What the state of combination of the potash may be is not certain.

The following composition of another slag affords a more striking illustration of the point under consideration. It was produced in the process of *puddling* in an iron forge.

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[1] Report on Crystalline Slags, by the author and W. H. Miller, M.A., F.R.S., &c., of Cambridge. British Association Reports for 1846.

		Oxygen.
Silica	23·86	12·41
Protoxide of iron	39·83	9·07
Sesquioxide of iron	23·75	7·28
Protoxide of manganese	6·17	1·38
Alumina	0·91	0·42
Lime	0·28	0·08
Magnesia	0·24	0·09
Phosphoric acid	6·42	3·60
Sulphide of iron	0·62	
	102·08	

Now this slag was well crystallized, and the crystals were found by Professor Miller of Cambridge closely to resemble olivine in their form; and, from the analysis of the crystals of another similar slag, which were measured, and which contained only 1·34 per cent. of phosphoric acid, there is no doubt that it originally consisted essentially of tribasic silicate of protoxide of iron. The phosphorus existed chiefly as phosphoric acid in combination with one or both oxides of iron, and in part possibly in the state of phosphide of iron; but in whatever state it was present, it must be regarded as *foreign* matter. If any phosphide of iron were present, the excess obtained in the analysis would be due in a certain degree to the oxidation of that phosphide during the process of analysis. The existence of the sesquioxide of iron admits of easy explanation. When silicate of protoxide of iron is heated to redness, with access of air, it increases in weight, owing to the absorption of oxygen; and the slag in question had, subsequently to its formation in the puddling furnace, been long exposed to this condition of oxidation, during which, no doubt, it absorbed oxygen with the partial conversion of the protoxide into sesquioxide of iron. The crystals must, therefore, be considered as pseudo-morphous. It will be shown in another part of this work that protoxide of iron in combination with silica in a slag of this kind may, by sufficiently long calcination, with access of air, be wholly converted into sesquioxide.

The base of a silicate may be displaced by another base having a greater affinity for silica, just as one base may be displaced by another in solutions of salts. Thus, Ebelmen found that oxide of iron might be completely separated from *refinery*-slag, of the formula $3FeO, SiO^2$, by lime. This slag was strongly heated with a piece of marble of its own weight in a platinum capsule during three days continuously. On removing the capsule from the furnace, it was found that the marble had entirely disappeared. The product, which was black, was treated first with cold dilute hydrochloric acid, and then with an alkaline solution to dissolve the gelatinous silica. The insoluble residue was a magnetic crystalline powder, which, under the microscope, was seen to consist of octahedral crystals of magnetic oxide of iron mixed with amorphous sesquioxide of iron: by digestion with strong hydrochloric acid it wholly dissolved, and the solution contained proto and sesquichloride of iron. The result was confirmed by a second experiment. Ebelmen made experiments of a similar kind

upon various borates, of which the results possess a high degree of interest. Thus, he obtained crystals of magnesia, of oxide of nickel, cobalt, and manganese, and of Perowskite (titanate of lime), of which he showed me beautiful crystals in the platinum capsule just as it had left the furnace.[2]

External characters.—Slags occur either more or less distinctly crystallized—in the state of glass—or non-crystalline and stone-like. A single piece of slag may present all these characters. Rapid cooling tends to produce the glassy state, and slow cooling the crystalline state. Hence, if a piece of slag is crystalline in one part and glassy in another, the outer part, which has been exposed to the air, or come in contact with the ground or other cooling surface, will always be the glassy one. In some slags isolated crystals are scattered through a glassy matrix—an appearance which may frequently be observed in slags from the blast-furnaces of South Staffordshire; in others, spheroidal masses, consisting of radiating fibrous crystals, and varying in diameter from that of a pea to an inch and upwards, are imbedded in a similar matrix; and in others again the whole mass is confusedly crystalline.[3] When glass—especially crown and bottle glass—is exposed to slow cooling during solidification from a state of fusion, or, after it has become cold and solid, is re-heated and kept for a long time at a high temperature, but below its fusing-point, it passes from the vitreous to the crystalline state, when it is said to be *devitrified.* The so-called porcelain of Réaumur is only devitrified glass. Common barley-sugar, which is sugar in a glassy state, the result of rapid cooling after melting, always becomes devitrified or crystalline on keeping, even at the ordinary temperature. Very beautiful and instructive illustrations of the crystallization of glass may be frequently obtained in glass-houses where either bottle or crown-glass is made; flint-glass, which is composed of silica, potash, and protoxide of lead, rarely occurs crystallized. In pieces of crown-glass the formation of crystals may be traced; little groups of delicate radiating prisms at first appear, which gradually increase in number and size until they finally coalesce into a white opaque mass. In bottle-glass the spheroidal masses are sometimes formed in parallel layers, closely resembling Lipari obsidian. Sections of devitrified glass are beautiful objects under the microscope, when seen by polarized light.

If a slag is a definite compound, it may, under favourable conditions of cooling, be converted into one mass of similar crystals; but if it is not a definite compound, crystals may be separated from the mass differing sensibly in composition from the original slag. The results obtained by Terreil in the investigation of devitrified glass illustrate these points. He examined bottle-glass which had been left to cool

[2] Recueil des Trav. Scient., I, p. 210. 1855.

[3] See an interesting paper "Sur la cristallisation des silicates vitreux, et sur la couleur bleue des laitiers." Par M. J. Fournet. Ann. de Ch. et de Phys., 3. s. 4, p. 370. 1842.

in the pots in consequence of repairs being required in the furnace. He analysed a specimen of crystallized or devitrified glass, and a specimen of transparent glass composed of the same materials and in the same proportion. The results are as follow:—

	Crystallized glass.	Transparent glass.
Silica	55·85	56·84
Lime	24·14	21·15
Magnesia	7·63	6·37
Alumina	2 22	3·64
Oxide of iron	1·06	2·59
Soda	8·47	8·69
Potash	0 63	0·40
Manganese	traces	traces
	100·00	100·00
Specific gravity	2·824	2·724

He analysed all the materials from which the glass was made, and calculated the composition from the proportions in which they were mixed, and found it to agree with that obtained by analysis; so that there was nothing lost during the process of devitrification. The oxygen of the silica is to that of the bases nearly as 9 : 4; whence he deduces the formula—

$$4RO, 3SiO^2.$$

R = CaO, MgO, NaO. Calculating from this formula, and neglecting the alumina and oxide of iron, the composition would be—

Silica	55·97
Lime	23·04
Magnesia	8·23
Soda	12·76

The crystals may be compared to natural *augite*, in which a portion of the magnesia is replaced by soda.

Terreil also analysed the crystallized and transparent portions in the same piece of glass. The results are as follow:—

	Crystallized glass.	Transparent glass.
Silica	63·67	63·43
Lime	18·65	18·14
Magnesia	6·12	4·47
Alumina	4·98	7·21
Oxide of iron	0·71	2·66
Alkalies	5·87	5·12
Manganese	traces	traces
	100·00	100·00
Specific gravity	2·610	2·857

The mixture used in the making of this glass differed from that used for the first. A fact first observed by Le Blanc is confirmed by these analyses, namely, the alumina and oxide of iron appear to become concentrated in the transparent glass—or, as it might be termed,

mother-liquor. In the last analyses the relation between the oxygen of the silica and that of the bases rather exceeds 9 : 4.[4]

Slags may be more or less *porous* or *vesicular*. I have found pieces of blast-furnace slag in South Staffordshire presenting a *cellular* structure, which in regularity might almost be compared to honeycomb. When blast-furnace slag is allowed to flow from the furnace into water, it swells up immensely, forming a white, very light, pumice-like mass. Occasionally specimens of slag may be obtained from blast-furnaces in the form of spun-glass. Owing to some accidental condition, the melted slag has actually been spun, as it were, by the blast, just as glass is spun by a wheel. I have received beautiful specimens of this kind from my friend Mr. Levick, of the Blaina and Cwm Celyn Iron-works, and also from Prussia.

In respect to *brittleness* and *toughness* there is great variation in slags. A slag will generally be tough in proportion to its slowness of cooling, just as devitrified glass, which is the result of slow cooling, is extremely tough as compared with the original glass. The slag which has been previously mentioned, and of which the formula is

$$R^2O^3, SiO^3 + 2\,(3RO, SiO^3),$$

is very brittle both in the crystallized and glassy state; whereas another crystallized slag from the same furnaces, of much less frequent occurrence, is extremely tough : its formula is

$$R^2O^3, SiO^3 + 3\,(2RO, SiO^3).$$

In both formulæ $R^2O^3 = Al^2O^3$ and $RO = CaO$, MgO, FeO, and MnO. I have not seen the last slag in a glassy state. When it is required to reduce slags to powder, as is frequently the case, it follows from the preceding considerations that a simple and effectual way of rendering them as brittle as possible is to cool them with great rapidity by allowing them to flow into water.

In respect to *colour*, slags of common occurrence are generally grey, blue, green, red, brown, or black, of various shades. Occasionally the same slag is beautifully veined or marbled, with varying shades of colour; and an attempt has been made to apply such slags to ornamental purposes, though unsuccessfully. The cause of the beautiful blue colour, which is not unfrequently seen in slags from iron-smelting furnaces, has excited much attention. It was ascribed to an oxide of titanium by Kersten, who also referred to the same oxide the blue coloration of the Silesian zinc-retorts, which is very similar to that of the slags in question. He found this oxide in the substance of which the retorts were made. He passed the vapour of zinc over titanic acid heated to redness, and the acid became blue. He then prepared mixtures of the ingredients of which slags are composed, and melted them; but the blue colour was not developed. When, however, they were kept melted at a strong heat in covered crucibles, with the addi-

[4] Note sur un verre à bouteille cristallisé. Par M. A. Terreil. Comp. Rend., 45, p. 693. 1857.

tion of a little titanic acid and zinc, tin, or iron, they became blue. The specimens thus produced were inspected by Berzelius, who regarded the proof as conclusive.[5] Fournet opposed the explanation of Kersten on the ground that certain slags, which were remarkable for the amount of titanium which they contained, were not blue, but grey in the interior and pale yellow on the surface; and that other slags, in which there was no reason to suspect the presence of titanium, were blue. He observed, moreover, that when common green bottle-glass is kept heated during a sufficient length of time at a temperature considerably below its melting-point, it was rendered opaque and acquired a blue colour similar to that of the slags. I had previously obtained the same result by experiment. Fournet had thin sections made of the glass so coloured, and found that when seen by transmitted light it had a greenish-yellow tint. D'Artigues had before ascertained the same fact. Fournet showed that the powder of the blue slags and blue glass had only a dirty green tint. By melting a silicate of iron and alumina Berthier obtained a glass which, by reflexion, presented a green, almost black tint, but which appeared resin-yellow by transmitted light.[6] From these considerations Fournet inferred that the blue coloration both in the slags and bottle-glass was entirely due to the same cause, namely, the same change in molecular arrangement which occasioned opacity in the bottle-glass.[7] Bontemps, who has had great experience in the manufacture of glass, and especially in its coloration, attributes the greenish colour of bottle-glass to oxide of iron combined with carbonaceous matters contained in the mixture. When the temperature is not very high, as, for example, in the covered pots in which flint-glass is made, oxide of iron gives a *green* colour, more nearly approaching yellow than blue; but when the temperature is high, as in the manufacture of window-glass, the addition of a small proportion of oxide of iron to the mixture produces a glass of a *bluish* colour. He also remarks that it is known to the manufacturers of bottle-glass, that when the glass is cooled in the pot it becomes opaque *blue* before being devitrified. He concludes from actual observation that glass may acquire all the colours of the spectrum from oxide of iron alone; and that these colours are produced in their natural order in proportion as the temperature increases. Thus the manufacturers of china and earthenware obtain a *purplish-red* from sesquioxide of iron at a certain temperature; and at a higher temperature the same oxide yields an *orange* colour. These temperatures are low as compared with that at which glass is melted; and, as has been stated above, the oxide renders glass *green* at one temperature and *blue* at a higher temperature.[8] The blue colour of slags has also been referred to vanadium[9] and artificial ultramarine. In respect to vanadium, it may be true that certain blue slags contain this metal, but no satis-

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[5] Jahres-Bericht, 2nd part, 20, p. 97. 1841.

[6] Traité des Essais, 1, p. 448.

[7] Op. cit. 4. p. 370.

[8] Inquiries on some modifications in the Colouring of Glass by Metallic Oxides. By G. Bontemps. Phil. Mag. 30, p. 439. 1849.

[9] Kersten, Ann. des Mines, 4. s. 2, p. 483. 1842.

factory proof has been advanced that it is the cause of their blue colour; and, in respect to ultramarine, I may state that in numerous experiments I have always found that the colour of ultramarine is destroyed at a temperature much below the fusing point of the compound of silicate of soda and alumina, which is termed ultramarine base. On a review of the evidence I am inclined to the belief that oxide of iron is the essential element of the blue colour of the slags.

Slags from iron-smelting furnaces have occasionally a very dark colour in mass, which might lead to the supposition that they contain a large proportion of iron. Analysis, however, has proved, as will be shown in the sequel, that this is not necessarily the case. It seems not improbable that this deep colour may in some cases be due to sulphur. In the French department of the Great Exhibition of 1851 were exhibited some vessels of glass remarkable for their intensely black colour, which Dumas assured me was produced entirely by the addition of sulphur. This is a subject which requires investigation. Berthier obtained a red glass of silicate of soda, the colour of which he supposed to be due to sulphide of sodium.[1]

Slags are occasionally met with which present exquisitely beautiful iridescence, quite equal to that so highly prized in certain kinds of pottery. In some, consisting chiefly of silicate of protoxide of iron, crystals of the tribasic silicate are imbedded, which are marked with coloured bands of great distinctness and beauty. In my collection I have many illustrations of this kind.

Fusibility.—This is a subject of great practical importance. When melted some are as liquid as water, and others are in a greater or less degree viscous. A particular degree of consistency may be essential to the success of a process in which the slag is separated from the subjacent metallic matter by skimming: if too thin, metallic matter is liable to be drawn out of the furnace along with the slag; and if too thick, it may not have properly subsided. In all cases in which the ores of valuable metals like copper, tin, &c. are smelted, the slags should be carefully inspected in order to ascertain that shots of metal are not retained in them. A slag is said to be *clean* or *not clean*, according as it is free or not free from mechanically-diffused metallic matter. Experiments were made some years ago by Smith and myself on the fusibility of various mixtures of silica with lime, and silica with magnesia. Generally plumbago crucibles brasqued[2] with anthracite powder were employed, as clay crucibles were found to be rapidly attacked, so that no certain results could be obtained. In experiments of a similar kind made long before by Berthier brasqued crucibles were also used. The silica was in the state of fine white sand, such as is used by glass-makers; the lime was prepared from Carrara marble slaked and re-heated so as to expel the water of hydration; it was thus obtained in a state of very fine divi-

[1] Tr. des Essais, 1. p. 425.

[2] Brasque is a French term applied to the carbonaceous lining of a crucible. (See article on Crucibles in the sequel.)

sion; the ingredients were well mixed by trituration in a mortar. The furnace employed, when not otherwise stated, was an air-furnace having a stack somewhat exceeding 60 feet in height; the fuel was anthracite; and a temperature sufficient to melt manganese could easily be obtained in this furnace.

No.	Numbers of the same Silicates in the tables succeeding.	Formula.	Ratio between the Oxygen of the Lime and the Oxygen of the Silica.	Weight in grains employed in each experiment.		Composition of the Mixture per cent.	
				Lime.	Silica.	Lime.	Silica.
1	25	$3CaO, SiO^3$....	1 : 1	1260	690	64·60	35·40
2	26	$3CaO, 2SiO^3$..	1 : 2	1260	1380	47·72	52·28
3	—	$2CaO, SiO^3$ ...	2 : 3	560	460	54·90	45·10
4	—	$9CaO, 4SiO^3$..	3 : 4	1008	736	57·79	42·21
5	23	$6CaO, SiO^3$....	2 : 1	896	245	78·50	21·50
6	—	$9CaO, 2SiO^3$..	3 : 2	756	276	73·25	26·75
7	27	CaO, SiO^3.....	1 : 3	840	1380	37·83	62·17

1. Exposed to a white heat during three hours; not melted. Some gelatinous silica was separated by the action of hydrochloric acid. Re-heated during an hour in Sefström's blast-furnace. Still not melted. Some dark grey melted particles were found in the mixture near the bottom of the crucible. A portion of this mixture was again exposed to a white heat during three hours; not melted. *Experiment repeated* with 840 of lime and 460 of silica. Exposed to a strong white heat during two hours; not melted. *Experiment repeated.* Exposed to a white heat during four hours and a half; not melted. *Experiment repeated.* Exposed to a white heat during three hours; not melted.

2. Exposed to a white heat during two hours and a half; well melted; compact, with a few large cavities in the centre; fracture glassy, lower part slightly crystalline. *Experiment repeated* in a Cornish crucible. Exposed to a white heat during two hours. The mixture formed a fused mass with the crucible. *Experiment repeated* in a Cornish crucible enclosed in another of the same kind. Exposed to a white heat during two hours and a half. The outer crucible was only little acted upon, but the inner one was melted into a clear glass with the mixture. *Experiment repeated* with 840 of lime and 920 of silica. Exposed to a white heat during four hours and a half; melted. The upper part contained large cavities lined with imperfectly defined crystals; lower part compact with a crystalline fracture. *Experiment repeated* with the same quantities. Exposed to a white heat during an hour; melted; crystallized in thin plates running in various directions; the transverse fracture presented the appearance of fibrous crystals radiating from the centre and intersecting each other at numerous points. The formula of this mixture is the same as that of tabular spar or Wollastonite.

3. Exposed to a white heat during two hours; melted. Com-

pact and slightly crystalline. *Experiment repeated* with 840 of lime and 690 of silica. Exposed to a white heat during four hours and a half. About one-sixth of the mixture near the bottom was melted; fracture crystalline.

4. Exposed to a white heat during an hour and a quarter; partly melted into lumps, which contained cavities lined with small imperfect crystals. *Experiment repeated* with 756 of lime and 552 of silica. Exposed to a white heat during two hours. A small portion near the bottom melted into a compact glassy slag; the rest not melted. *Experiment repeated* with the same quantities. Exposed to a white heat during four hours and a half; not melted. *Experiment repeated* with the same quantities. Exposed to a white heat during two hours and a half; not melted. Mixture adhered together, but crumbled under very slight pressure. *Experiment repeated.* Exposed to a white heat during two hours and a half; about one-third melted at the bottom. Compact, with crystalline fracture.

5. Exposed to a white heat during an hour and a half; not melted. *Experiment repeated.* Exposed to a white heat during two hours; not melted.

6. Exposed to a white heat during an hour and a half; not melted. *Experiment repeated.* Exposed to a white heat during two hours; not melted. *Experiment repeated.* Exposed to a white heat during two hours; not melted.

7. Exposed to a white heat during an hour and twenty minutes; about two-thirds melted into a compact glassy slag, the upper part containing small cavities lined with little crystals; surface of mixture not melted. *Experiment repeated.* Exposed to a white heat during two hours and a half; not melted. The same mixture was further exposed to a white heat during five hours; about half the mixture melted into a porous crystalline mass; the rest not melted, but adhered together. *Experiment repeated.* Exposed to a white heat during three hours; not melted. The same mixture was further exposed to a white heat during two hours and three-quarters; well melted. Compact, with a few small cavities near the surface.

The magnesia which was employed in the following experiments was prepared by calcination of the carbonate.

No.	Numbers of the same Silicates in the tables succeeding.	Formula.	Ratio between the Oxygen of the Magnesia & the Oxygen of the Silica.	Weight in grains employed in each experiment.		Composition of the mixture per cent.	
				Magnesia.	Silica.	Magnesia.	Silica.
1	30	$3MgO, SiO^3$ ..	1 : 1	756	552	57·79	42·21
2	31	$3MgO, 2SiO^3$..	1 : 2	756	1104	40·64	59·36
3	—	$2MgO, SiO^3$ ...	2 : 3	756	828	47·72	52·28
4	—	$9MgO, 4SiO^3$.	3 : 4	756	736	50·67	49·33
5	29	$6MgO, SiO^3$ ...	2 : 1	756	276	73·25	26·75
6	—	$9MgO, 2SiO^3$..	3 : 2	756	368	67·25	32·75
7	32	MgO, SiO^3 ...	1 : 3	756	1656	31·34	68·66

1. Exposed to a white heat during two hours; imperfectly fused into a white, hard, porous, slightly-crystalline mass.

2. Exposed to a white heat during an hour; about one-sixth of the mixture near the bottom was melted into a hard crystalline mass; the rest consisted of a partially-melted, hard, slightly-crystalline mass, passing into a *frit* near the top—that is, a mass more or less sintered or fritted together. The crucible, with its contents, was again exposed to a white heat during an hour; the portion previously unmelted was now melted, yet not so completely as the portion first melted, of which the pieces could be readily recognised.

3. Exposed to a white heat during two hours; melted. Compact, with a few cavities in the centre; fracture crystalline.

4. Exposed to a white heat during two hours; melted. Hard, porous, with traces of crystallization.

5. Exposed to a white heat during two hours; not melted, but fritted.

6. Exposed to a white heat during two hours; melted. Largely porous.

7. Exposed to a white heat during two hours; melted. Hard, porous, slightly crystalline.

The result of the very numerous experiments of Berthier on the fusibility of mixtures consisting of silica and various bases will be found in the following tables (pp. 33—37). The tabular form has been selected in order to facilitate reference. In the description of the character of the products I have, as far as practicable, adhered to the precise language of Berthier.

Berthier has interspersed through the descriptions of his experiments a series of deductions, which, on account of their interest or practical importance, I now introduce.

1. Weight for weight, soda fluxes[3] more than potash.

2. The alkaline silicates never acquire a stony aspect, and always produce glasses without any indication either of crystallization or of lamellar structure, whether rapidly cooled or left to cool slowly as in a porcelain-furnace.

3. Only those silicates of baryta fuse well which contain less baryta than $3BaO,2SiO^3$, and less silica than $BaO,4SiO^3$.

4. Strontian is less fluxing than baryta.

5. No silicate of alumina is completely fusible at the highest temperature of our furnaces, but some of them soften, and all are more or less strongly agglomerated. The silicates of alumina $Al^2O^3,2SiO^3$, and $Al^2O^3,3SiO^3$ appear to soften most of all. Their tendency to fuse may be diminished by the addition either of silica or alumina.

6. Amongst the alkalies, alkaline earths, and earths, the fluxing property in respect to silica increases or decreases with the chemical force of the base. It is to be observed that the solubility in water follows

[3] The verb *to flux* is in common use amongst metallurgists and the workers in metals.

No.	FORMULA.	Potash.	Soda.	Baryta.	Strontian.	Lime.	Magnesia.	Protoxide of Iron.	Protoxide of Manganese.	Alumina.	Silica.
1	KO, SiO^3	50·5	..	..	..	..	..	..	..	..	49·5
2	KO, $2SiO^3$	33·8	..	..	..	..	..	..	..	..	66·2
3	KO, $3SiO^3$	25·4	..	..	..	..	..	..	..	..	74·6
4	KO, $4SiO^3$	20·3	..	..	..	..	..	..	..	..	79·7
5	KO, $6SiO^3$	14·3	..	..	..	..	..	..	..	..	85·7
6	KO, $10SiO^3$	9·0	..	..	..	..	..	..	..	..	91·0
7	NaO, SiO^3	40·2	..	..	..	..	..	..	..	..	59·8
8	NaO, $2SiO^3$	25·2	..	..	..	..	..	..	..	..	74·8
9	NaO, $3SiO^3$	18·3	..	..	..	..	..	..	..	..	81·7
10	NaO, $4SiO^3$	14·4	..	..	..	..	..	..	..	..	85·6
11	NaO, $6SiO^3$	..	9·9	..	..	..	..	..	..	..	90·1
12	NaO, $8SiO^3$	..	7·6	..	..	..	..	..	..	..	92·4
13	NaO, $10SiO^3$	..	6·2	..	..	..	..	..	..	..	93·8
14	3BaO, SiO^3	..	..	82·3	..	..	..	..	..	..	17·2
15	3BaO, $2SiO^3$	..	..	70·7	..	..	..	..	..	..	29·3
16	BaO, SiO^3	..	..	61·6	..	..	..	..	..	..	38·4
17	BaO, $2SiO^3$	..	..	44·5	..	..	..	..	..	..	55·5
18	BaO, $3SiO^3$	..	..	34·8	..	..	..	..	..	..	65·2
19	BaO, $4SiO^3$	..	..	28·5	..	..	..	..	..	..	71·5
20	3SrO, $4SiO^3$	..	..	..	44·9	..	..	..	..	..	55·1
21	SrO, $3SiO^3$	..	..	..	26·5	..	..	..	..	..	73·4
22	12CaO, SiO^3	..	..	..	..	88·5	..	..	..	..	11·5
23	6CaO, SiO^3	..	..	..	..	78·0	..	..	..	..	22·0
24	4CaO, SiO^3	..	..	..	..	70·3	..	..	..	..	29·7
25	3CaO, SiO^3	..	..	..	..	64·2	..	..	..	..	35·8
26	3CaO, $2SiO^3$	..	..	..	..	47·2	..	..	..	..	52·8

REMARKS.

B. abbreviation for Berthier.
G. f. „ air-furnace capable of producing 150° pyrometer of Wedgwood (p.) in 2 hrs.
S. „ porcelain-furnace at Sèvres, which Berthier estimates at 140° p.

It must be borne in mind that Berthier's work was published in 1834, and that the equivalent weights which he employed were those adopted by Berzelius at the time.

1, 2, 3, 4. Transparent glass, containing more or less bubbles. At 50° p. 3 parts of carbonate of potass or soda form a very liquid compound with silica: at 150° only a very small quantity of alkali is sufficient to produce this effect. B.

5. Transparent colourless glass, but very full of bubbles. B.

6. Transparent glass, but scoriaceous, occupying the same volume as the original silica. B.

7, 8, 9, 10. Transparent glass, compact, or containing more or less bubbles. B.

11, 12. Transparent glass, but very full of bubbles. B.

13. Enamel, white, scoriform, slightly translucent, occupying the same volume as the materials employed. B.

14. (G. f. and S). Agglomeration and commencement of pasty fusion. B.

15. (S). Button compact, a little bubbly on the surface, fracture scaly and waxy. B.

16. (S). Button free from bubbles, tender, fracture crystalline, fragments translucent, shining. B.

17, 18 (S). Compact, translucent, fracture conchoidal, slightly waxy. B.

19. (G. f.) Enamel, white, porous, hard, opaque or slightly translucent; imperfect fusion. B. These silicates were prepared with sand and native carbonate of *baryta*.

20. (G. f.) Enamel, white, compact, free from bubbles, transparent in some parts, but throughout hardly translucent at the edges, fracture slightly conchoidal, shining. B.

21. (G. f.) Slightly enamel-like, scoriform, full of cavities like a sponge, slightly translucent: no fusion. B. These silicates were prepared with sand and artificial carbonate of strontia.

22, 23, 24. Pulverulent. B.

25. Partly scoriform and partly pulverulent: incipient fusion. B.

26. (S). Slightly bubbly, aspect stony, fracture granular; in cavities brilliant, distinct but very small crystals may be observed. B.

(G. f.) Scoriform and half-glassy in the course of 1 hour; heated during 2 hours, partly compact and partly bubbly, translucent, fracture waxy, slightly shining. B. This has the same formula as *Tabular-Spar* or *Wollastonite*.

No.	FORMULA.	Potash.	Soda.	Baryta.	Strontian.	Lime.	Magnesia.	Protoxide of Iron.	Protoxide of Manganese.	Alumina.	Silica.	REMARKS.
27	CaO, SiO^3	..	..	..	..	37·8	..	..	..	..	62·2	27. (S). Button scoriform, beautiful white, translucent, resembling porcelain; fracture uneven, finely granular; scratches glass. B.
28	$3CaO, 4SiO^3$	..	..	..	..	24·4	..	..	..	..	75·6	28. (S). Scoriform, translucent, without solidity, gritty between the fingers.—(G. f.) Transparent porous glass. B.
29	$6MgO, SiO^3$	..	..	..	..	..	72·2	..	..	..	27·8	29, 30. (S). Compact, with but little tenacity, easily crushed, yet hard enough to scratch glass; fracture uneven, granular, dull: combination without softening, as gelatinous silica was separated by acids. B.
30	$3MgO, SiO^3$	..	..	..	..	..	56·5	..	..	..	43·5	
31	$3MgO, 2SiO^3$	..	..	..	..	..	40·1	..	..	..	59·9	
32	MgO, SiO^3	..	..	..	..	..	30·0	..	..	..	70·0	
33	$2Al^2O^3, SiO^3$	..	..	..	..	..	..	..	..	64·3	35·7	31. (G. f.) Strongly agglomerated, stony, very hard, slightly porous, fracture granular, almost smooth: softening without fusion. B.
34	Al^2O^3, SiO^3	..	..	..	..	..	..	..	..	52·6	47·4	
35	$Al^2O^3, 2SiO^3$	..	..	..	..	..	..	..	..	35·7	64·3	
36	$Al^2O^3, 3SiO^3$	..	..	..	..	..	..	..	..	27·0	73·0	
37	$KO, NaO, 10SiO^3$	8·7	5·8	..	..	..	..	..	..	..	85·5	32. (S). Button solid, tenacious, scratches glass; fracture compact, stony, dull; full of round pores: incipient fusion. B.
38	$KO, NaO, 20SiO^3$	4·7	2·9	..	..	..	..	..	..	..	92·4	
39	$KO, Al^2O^3, 4SiO^3$	16·31	..	..	..	..	..	..	..	17·75	65·94	33, 34. (S). Agglomerated. B.
40	$NaO, Al^2O^3, 4SiO^3$	..	11·43	..	..	..	..	..	..	18·79	69·72	35. (S). Strongly agglomerated, compact; fracture stony, dull. B.
41	$3KO, 5Al^2O^3, 22SiO^3$	8·4	..	..	..	..	..	..	..	16·2	73·0	36. (G. f.) Compact; fracture stony, slightly shining. B. These silicates of alumina were prepared with sand and calcined sulphate of alumina.
42	$BaO, 11CaO, 8SiO^3$	..	..	10·0	..	41·4	..	..	..	..	48·6	37. Glass, homogeneous, transparent, bubbly in places. B.
43	$BaO, 5CaO, 8SiO^3$	..	..	24·8	..	12·1	..	..	..	..	63·1	38. Glass, homogeneous, transparent, and penetrated throughout with a multitude of minute bubbles. B.
44	$3BaO, 6Al^2O^3, 14SiO^3$	..	..	19·0	..	..	..	..	..	26·0	55·0	39, 40. (S. and G. f.) Transparent glass always filled with a multitude of minute bubbles. No. 39 is felspar,—*orthoclase*. No. 40 is also felspar,—*oligoclase*. B.
45	$3BaO, 4Al^2O^3, 12SiO^3$	..	..	22·7	..	..	..	..	..	20·3	57·0	
46	$3CaO, 3MgO, 2SiO^3$	..	..	..	..	35·5	25·5	..	..	..	39·0	
47	$3CaO, 3MgO, 4SiO^3$	..	..	..	..	25·3	18·3	..	..	..	56·4	

41. (S). This is the glaze used for porcelain at Sèvres; it melts on the biscuit into a colourless enamel glass; in a brasqued crucible it melts into a glass containing large bubbles. B.

42. (G. f.) Compact, free from bubbles, transparent, fracture lamellar in one direction, but in other directions uneven and scaly. B.

43. (G. f.) Compact, free from bubbles, translucent, fracture largely concholdal, brilliant, resembling beautiful chalcedony. B.

44, 45. (S). Compact, free from bubbles; fracture even and shining, vitreous in places, presenting no indication of crystallization. No. 44 is identical with *harmotome*. B.

46. (S). Compact, with a fine scaly close grain; thin fragments translucent. B.

47. (S.) Melts easily into a compact lamellar mass, with large plates or long prismatic fibres; the surface covered with polyhedral asperities, which are only the summits of the fascicular prisms of which it is composed. In several experiments the button contained a cavity lined with beautiful transparent crystals several millimètres broad. The button is somethnes saccharoidal instead of lamellar, but never vitreous. This is identical with augite or pyroxene. B. When melted with 6 per cent. of fluor-spar in powder, a button was obtained composed of large interlacing crystals, having spaces between them. The crystals were transparent or translucent, slightly greenish, brilliant, from 2 to 3 centimetres long and several millimetres broad, with well-defined terminations. It was also melted with 30 per cent. of dry chloride of sodium, in the hope that the compound would crystallize regularly in a fused matrix of chloride. On treating the product broken into small pieces with water, much chloride of calcium was dissolved, and the residue, which became porous, pre-

No.	FORMULA.	Potash.	Soda.	Barytn.	Strontian.	Lime.	Magnesin.	Protoxide of Iron.	Protoxide of Manganese.	Alumina.	Silica.	REMARKS.
48	$CaO, 2MgO, 2SiO^3$ ...	..	..	..	..	17·3	25·2	..	..	..	57·5	sented a *multitude of well defined but always* extremely small crystals. When augite is melted in an air-furnace, and when, consequently, cooling takes place rapidly, the mass is sometimes saccharoidal; but it never presents crystals, and most frequently it is compact and vitreous. B. This idea of obtaining crystals in a matrix fusible at a strong heat is similar in principle to that which Ebelmen long afterwards adopted with so much success in the formation of various crystals, Ebelmen replacing chloride of sodium by boracic acid or borax.
49	$2CaO, MgO, 2SiO^3$ ...	..	..	..	..	33·5	12·1	..	..	..	54·4	
50	$CaO, 3MgO, 3SiO^3$ ...	..	..	..	..	9·3	20·3	..	..	..	70·4	
51	$CaO, MgO, 2SiO^3$.....	..	..	..	..	19·8	14·0	..	..	..	66·2	
52	$2CaO, MgO, 4SiO^3$ ...	..	..	..	..	21·2	7·7	..	..	..	71·1	
53	$CaO, 2MgO, 4SiO^3$ ...	..	..	..	..	10·9	15·8	..	..	..	73·3	
54	$3CaO, Al^2O^3, SiO^3$ ...	..	..	..	..	46·3	..	..	..	27·8	25·9	
55	$3CaO, Al^2O^3, 2SiO^3$ ...	..	..	..	..	35·8	..	..	..	22·0	41·0	
56	$3CaO, Al^2O^3, 4SiO^3$...	..	..	..	..	26·1	..	..	..	15·7	58·2	
57	$3CaO, Al^2O^3, 6SiO^3$...	..	..	..	..	20·2	..	..	..	12·1	67·7	
58	$3CaO, 2Al^2O^3, 3SiO^3$	..	..	..	..	26·0	..	..	..	31·3	43·7	
59	$3CaO, 3Al^2O^3, 4SiO^3$	..	..	..	..	19·9	..	..	..	35·8	44·3	
60	$CaO, Al^2O^3, 4SiO^3$ ...	..	..	..	..	10·5	..	..	..	19·0	70·5	
61	$6CaO, Al^2O^3, 3SiO^3$...	..	..	..	..	47·3	..	..	..	14·2	38·4	

50. (S). Melted with 30 per cent. of chloride of calcium, it gave a compact mass, white, crystalline, resembling Carrara marble: after having been broken up and digested with water, it presented a very lamellar structure, and here and there little pearl-white prisms, sometimes fasciculated and sometimes grouped in different ways, but of which none had a termination. When the same mixture was melted (S.) with 3·3 per cent. of fluor-spar, a very beautiful white button was obtained, compact, very hard; fracture crystalline in some parts and presenting in others radiated bundles, composed of acicular prisms, which could not be measured. B.

51. (S). Button scoriform on the surface, but compact in the centre; fracture uneven, granular, opaque; it could not have been very liquid. B.

52. (S). Melted into a compact mass, free from bubbles, hard, tenacious, opaque, stony; fracture uneven, presenting scarcely any indication of crystalline structure. B.

53. (S). Melted into a button slightly bubbly, translucent; fracture granular, presenting some crystalline points. B.

54. (S). Button contained cavities, in which were pulvegulent grains, a sign that the matter was not homogeneous and, consequently, that it had not been fully melted. B.

55. (S). Perfectly melted, porcelain-white, very hard, opaque; fracture uneven, dull, in which here and there very small crystalline grains could be distinguished, but the form of *garnet* could not be recognised. The same compound melted with 7·5 per cent. of fluor-spar (S.) gave a compact button, free from bubbles,—in part glassy and quite transparent, and in part translucent and waxy, but without the least appearance of crystallization: it resembled hydrophane. Treated with chloride of calcium, it gave a compact button without any appearance of crystallization; but which, after having been washed, presented in the centre of the mass a multitude of very brilliant small crystals. With its own weight of chloride of barium, it gave a compact, slightly crystalline button, resembling white marble, and which, after having been washed, presented a very decided crystalline structure, but there were no regular crystals. B.

56. (S). Button compact, free from bubbles, white, slightly translucent, fine-grained and lamellar. It is very fusible, and vitreous when rapidly cooled. B.

57. (S). Button filled with cavities, stony; fracture uneven, granular, opaque, and of a beautiful white. B.

58. (S). Button compact, free from bubbles; fracture uneven, granular, opaque, presenting no sign of crystallization. B.

59. (S). Button filled with large cavities, opaque; fracture uneven, granular, dull, without sign of crystallization. B.

60. (S). Melted into a compact button, stony, opaque; fracture saccharoidal; the grains were very distinctly crystallized and transparent. B.

61. (S). Button compact, free from bubbles, very tenacious; fracture uneven, thin fragments translucent, resembling compact quartz, without sign of crystallization. B. This is identical in composition with a

No.	FORMULA.	Potash.	Soda.	Baryta.	Strontian.	Lime.	Magnesia.	Peroxide of Iron.	Protoxide of Manganese.	Alumina.	Silica.	REMARKS.
62	.. ..	..	..	..	..	60·0	..	..	..	13·5	26·5	crystallized slag which frequently occurs in South Staffordshire, and of which an analysis has been given.(p. 23).
63	.. ..	..	..	..	..	52·8	..	..	..	16·0	31·2	62. (G. f.) Remained quite pulverulent. B.
64	.. ..	..	..	..	..	48·3	..	..	..	17·6	34·1	63. (G. f.) Button stony and tenacious to the depth of 1 or 2 millimetres; but the centre was pulverulent. B.
65	.. ..	..	..	..	..	60·0	..	..	..	6·7	33·3	64. (G. f.) Melted into a compact mass, free from bubbles, very tenacious; fracture waxy, a little shining. B.
66	$3MgO, Al^2O^3, 2SiO^3$...	..	..	..	..	..	29·3	..	..	24·8	45·9	65. (G. f.) About the same as No. 64. B.
67	$3MgO, Al^2O^3, 4SiO^3$...	..	..	..	..	..	20·0	..	..	17·0	63·0	66. (S). Button compact, stony, opaque; fracture even or uneven, slightly shining. B.
68	$6FeO, SiO^3$	..	..	..	..	..	..	82·0	..	..	18·0	67. (S). Like No. 66; fracture uneven, dull. Both Nos. 66 and 67 completely melted. B.
69	$3FeO, SiO^3$	..	..	..	..	..	..	69·0	..	..	31·0	68. Bubbly; finely granular in one part, and confusedly crystalline in another; cavities lined with microscopic crystals. B.
70	$3FeO, 2SiO^3$	..	..	..	..	..	..	52·5	..	..	47·5	69. Very easily melted; mass lamellar, with large intersecting cleavage-planes, very brilliant, deep olive-grey; on the surface is seen an indication of crystallization in rectangular prisms. B. This compound perforates a clay crucible with great rapidity. It not unfrequently occurs beautifully crystallized in refinery and puddling-furnace slags. It is *olivine* in which the magnesia is wholly replaced by protoxide of iron.
71	FeO, SiO^3	..	..	..	..	..	..	42·5	..	..	57·5	70. Melted into a compact mass; fracture uneven, presenting only in some places indications of crystallization; colour pale-olive and greyish. B.
72	Fe^2O^3, SiO^3	..	..	..	..	..	..	62·3	..	..	37·7	71. Melted into a compact homogeneous mass; fracture
73	$Fe^2O^3, 2SiO^3$	..	..	..	..	..	..	45·3	..	..	54·7	
74	$3FeO, 3CaO, 2SiO^3$...	..	..	..	..	29·9	..	36·4	..	..	33·7	
75	$2FeO, CaO, SiO^3$	..	..	..	..	19·6	..	47·5	..	..	32·9	
76	$3FeO, 3CaO, 4SiO^3$...	..	..	..	..	22·0	..	28·0	..	..	50·0	
77	$3FeO, 12MgO, 5SiO^3$	..	..	..	..	..	42·2	17·5	..	..	40·3	
78	$3FeO, Al^2O^3, 2SiO^3$...	..	..	..	..	..	..	42·0	..	20·4	37·6	
79	$Fe^2O^3, 3CaO, 2SiO^3$...	..	..	..	..	33·3	..	30·6	..	..	36·1	
80	$Fe^2O^3, Al^2O^3, 2SiO^3$...	..	..	..	..	..	..	38·8	..	25·5	35·7	

Peroxide of Iron / Protoxide of Manganese: Sesquioxide

Peroxide of Iron: Protoxide.

Peroxide of Iron: Sesquioxide

uneven or conchoidal, shining, opaque, olive-grey; is without action on the magnet. This silicate was melted in a clay crucible without traversing it. B. These silicates were prepared in wrought-iron crucibles enclosed in clay crucibles.

72, 73. The mixtures did not decrease in volume: there was no combination. The buttons were tenacious, of a deep grey colour, and magnetic; their powder was red, and grains of oxide of iron might be distinguished in it, of which the surface was metalloid in appearance. Berthier supposed that they had been reduced to magnetic oxide by the gases of the furnace. B.

74. Compact; presenting brilliant cleavages in some parts, and on the surface radiated crystallization like sulphide of antimony. B.

75. Compact, free from bubbles, strongly magnetic; fracture uneven, vitreous or crystalline, presenting confusedly radiated bundles. B.

76. Similar to No. 75. B.

77. Perfectly melted, porous, opaque, presenting no sign of crystallization. B.

78. Melted in a clay crucible into a compact mass, free from bubbles, extremely tenacious; fracture slightly conchoidal or waxy, shining, only translucent on the edges; by reflexion it appeared green, almost black; but when seen by transmitted light in thin lamina, it had the colour of resin (see p. 28); it scarcely affected the magnet; although it had been very liquid, it had not attacked the crucible. B.

79. Melted in a clay crucible into a compact black glass; fracture largely conchoidal, very brilliant; scarcely translucent on the edges; yellowish-brown in thin slices, without action on the magnet; half the matter had passed through the crucible. B.

80. Appeared to have only been in the pasty state; contained a large cavity in the centre; blackish-grey in

No.	FORMULA.	Potash.	Soda.	Baryta.	Strontian.	Lime.	Magnesia.	Sesquioxide of Iron.	Protoxide of Manganese.	Alumina.	Silica.	REMARKS.
81	Fe^2O^3, Al^2O^3, $4SiO^3$...	..	..	..	..	..	..	24·0	..	16·0	60·0	the centre; fracture uneven, opaque; in contact with the crucible vitreous, brilliant but opaque, very strongly magnetic; it had not attacked the crucible. B.
82	$6MnO$, SiO^3	..	..	..	..	..	..	..	82·0	..	18·0	81. Completely melted into a brilliant black glass, very hard and tenacious, slightly bubbly, fracture conchoidal, shining, opaque even in the thinnest slices; powder black without any red tinge, strongly magnetic; it had not attacked the crucible. B. Berthier concluded that some protoxide was formed by the reducing action of the gases of the furnaces; but I think it probable that the same result might occur without. Thus when silica and black oxide of copper are heated together in a muffle, in which the atmosphere is highly oxidizing, there is always reduction to di-oxide.
83	$3MnO$, SiO^3	..	..	..	..	..	..	..	66·2	..	33·8	
84	$3MnO$, $2SiO^3$.....	..	..	..	..	..	..	..	53·4	..	46·6	
85	$3MnO$, $4SiO^3$.....	..	..	..	..	..	..	..	36·0	..	64·0	
86	$3MnO$, $3CaO$, $4SiO^3$...	..	..	..	..	23·6	..	..	26·7	..	49·7	
87	MnO, $2CaO$, $2SiO^3$ ...	..	..	..	..	30·6	..	..	19·6	..	49·8	
88	$4MnO$, $4CaO$, $6SiO^3$...	..	..	..	..	20·8	..	..	26·8	..	52·4	
89	MnO, $2CaO$, $3SiO^3$ ...	..	..	..	..	24·0	..	..	15·5	..	60·5	
90	$3MnO$, $12CaO$, $22SiO^3$	..	..	..	..	22·3	..	..	7·1	..	70·6	
91	$3MnO$, $3MgO$, $2SiO^3$	..	..	..	..	..	22·7	..	41·2	..	36·1	
92	$3MnO$, $3MgO$, $4SiO^3$	..	..	..	..	..	17·0	..	30·4	..	52·6	
93	$2MnO$, MgO, $2SiO^3$...	..	..	..	..	..	11·1	..	40·0	..	48·9	
94	$3MnO$, $2Al^2O^3$, $4SiO^3$	..	..	..	..	..	..	..	27·5	25·8	46·7	
95	$3MnO$, $12CaO$, $22SiO^3$	..	..	..	..	..	..	..	19·0	23·3	57·0	
								Protoxide.				
96	$3FeO$, $3MnO$, $4SiO^3$...	..	..	..	..	..	..	26·0	27·0	..	47·0	82. (S). Melted into a compact mass, dull green, fracture somewhat lamellar, very fragile, appeared to be here and there mixed with brown oxide of manganese; when broken in small pieces and breathed upon, there was the odour of hydrogen, yet no metallic grains could be perceived. B.
												83. (S). Melted into a compact button, free from bubbles and without the least vitreous appearance, greyish-

green, lustre fatty, strongly translucent, cleavage in various directions, in large brilliant plates having the form of peridot. Melted (G. f.) it gave an olive-green button, opaque or scarcely translucent on the edges, having in the centre a large cavity filled with the rudiments of large crystals; there was a little grain of metallic manganese weighing $\frac{1}{200}$ of the weight of the mass. B.

84. (S). Button pale flesh-red, opaque or scarcely translucent, free from bubbles, lamellar throughout, with large very brilliant intersecting plates; this structure rendered it very fragile; it must have been very liquid. B.

85. (S). Button scoriform, filled with cavities, easily crushed between the fingers owing to its structure, but very hard, strongly scratched glass; fracture granular and dull through the greater part of the mass, lamellar in some points, opaque, aspect earthy, green externally, and clear pale brown (blond) in the interior; the matter must have been softened, but not completely melted. B.

86. (S). Button perfectly melted, very clear grey, slightly translucent, fracture uneven and a little waxy, presenting here and there signs of crystallization in prisms. (G. f.) It gave a compact button, free from bubbles, fracture largely conchoidal and shining, transparent and smoky (couleur enfumée). B.

87. (S). Button compact, free from bubbles, colourless or of a slightly olive-grey, strongly translucent, lustre pearly, fracture curved lamellar, entirely composed of fasciculated not very distinct prisms; but the crystallization was very apparent on the surface from the terminations of the prisms. B.

88. (S). Button compact, slightly translucent, colour varying from asparagus-green to yellow-brown (jaune-blond), very lamellar, plates fibrous twisted (contournées). B.

89. (S). Button very well melted, fragile, largely lamellar, strongly translucent, slightly greenish. B.

90. (S). Button scoriform, and grey externally, compact with a few bubbles in the interior, fracture lamellar or scaly, white brilliant and translucent; there must have been complete fusion, without great liquidity. B.

91. (S). Button well rounded, compact, without the slightest bubble, clear grey, fracture stony dull. B.

92. (S). Button like No. 91; fracture lamellar: the plates were lustrous and translucent. In another experiment the button was scoriform and bubbly, scarcely translucent on the edges. B.

93. (S). Button compact, free from bubbles, grey or a little greenish, slightly translucent, fracture uneven, waxy, feebly shining, presenting here and there microscopic crystalline particles. B.

94. (S). Button compact, free from bubbles, fracture rough (raboteuse), glassy, shining, clear olive-green in the greater part; granular, greyish and opaque in other parts, very tenacious, without any sign of crystallization. B.

95. (G. f.) Button rounded, compact, almost free from bubbles, fracture vitreous brilliant, olive-green, scarcely translucent at the edges; the fusion must have been a little pasty. B.

96. Heated in an iron crucible, well melted, homogeneous, but very bubbly, fracture uneven and dull, aspect stony, very clear grey, without any sign of crystallization. B.

follows the same order, and probably the same is true of the fusibility proper to each base.

7. Amongst the simple metallic silicates the fusibility is proportionate to the chemical energy of the oxide. But this relation ceases when we compare bases of different classes; for example, the alkalies, alkaline earths, and earths with metallic oxides. Thus oxide of lead is infinitely more fluxing than baryta, although it is separated from all its combinations by baryta. The relation, however, does not always hold good with metallic oxides not very remote from each other. Thus oxide of zinc is a powerful base, and produces a comparatively infusible silicate, whereas protoxide of iron produces a remarkably fusible silicate.

8. The fusibility of simple silicates appears to depend on three causes—the fusibility proper to each base; its chemical energy; and the proportion in which it enters into the compound.

9. With respect to double and multiple silicates, their fusibility depends upon that of the elementary silicates. A silicate which is infusible *per se* may always be melted by combining it with a proper quantity of a fusible silicate. It appears, even, that the fusibility of multiple silicates is greater than that of the mean of the component silicates; for many infusible, or difficultly fusible, silicates may, in combining with each other, form very fusible double silicates; for example, silicate of lime and magnesia, of lime and alumina, &c.

10. The alkaline silicates always give great fusibility to the compounds which they form with other silicates. It is remarkable that compounds containing a somewhat considerable proportion of alkali preserve, like the alkaline silicates, their vitreous aspect when cooled very slowly, and they do not then acquire the stony aspect and crystalline structure, as is the case with most of the other silicates.

11. Potash and soda, when mixed together, are more fluxing than each alkali separately.

12. When a simple or multiple silicate, containing a somewhat large proportion of alkali, is heated with a fixed and irreducible base, this base sets free part of the alkali, which volatilizes. Thus 15 grammes of silicate of soda—containing, of silica 10·35, and of soda 4·65—were heated (G. f.) with 5·6 of lime: a button was obtained which weighed only 19·2; so that 1·4 of soda had been volatilized. The button was compact, free from bubbles, opaque, with a stony fracture, somewhat shining. There is no doubt that volatilization of alkali is effected on this principle in blast-furnaces.

13. A clay, of whatever kind, always melts into glass when heated to 150° p. with half its weight of carbonate of potash or soda; part of the carbonate infiltrates into the brasque before combination occurs, and there remains in the melted product only about 12 to 15 per cent. of its weight.

14. Lime, which forms only infusible or very difficultly fusible compounds with silica, may produce, with a great number of infusible or slightly fusible silicates, compounds which melt easily.

15. Amongst the compounds which silica may form with lime and

alumina the most fusible are comprised between those in which the oxygen of the silica is double the sum of that of the lime and alumina and those in which the oxygen of the silica is half the sum of that of the lime and alumina; and these compounds are fusible in proportion as the relation between the bases approaches that of $6CaO : Al^2O^3$. They still melt well when the relation is $3CaO : Al^2O^3$, but they become much less fusible when the relation is $3CaO : 2Al^2O^3$. The composition of clays which are richest in alumina may, with some exceptions, be expressed by the formula $Al^2O^3, 2SiO^3$. Hence it follows that, by the addition of an amount of carbonate of lime intermediate between 3CaO and 6CaO, or the equivalent in carbonate of lime, they ought always to melt well; and that the fusion ought to be still more easy when in addition to lime silica is also added in a proportion ranging from SiO^3 to $4SiO^3$. But the addition of silica is almost always superfluous, because clays are rarely free from admixture with quartzose sand. Any clay whatever may be rendered sufficiently fusible by the addition of from half to three-quarters of its own weight of carbonate of lime to allow shots of metal to sink through the mass and collect into a button at the bottom. When, as sometimes happens, clays are mixed with hydrate of alumina, it becomes necessary to add at the same time silica and lime. The addition of a small proportion of different bases greatly increases the fusibility. Thus the silicate composed of

Silica	38·0
Lime	50·0
Alumina	6·5
Magnesia	2·0
Protoxide of manganese	3·5

melts into a compact enamel-like mass, of a greenish colour, here and there lamellar, but which is sufficiently liquid to allow shots of metal to pass through it.

16. Magnesia may, like lime, cause the fusion of the silicates of alumina, but it is much less fluxing.

Sefström's experiments on the formation of certain silicates of lime, magnesia, and alumina.[4]—These experiments were made by the students of the School of Mines at Fahlun under the direction of Sefström. The mixtures were exposed in crucibles lined with charcoal to the heat of a Sefström's blast furnace, in which wrought iron, manganese, and pure nickel could be melted. The numbers in the following description refer to those in the tables pp. 33-37.

$3CaO, 2SiO^3$. No. 26.—Pure white marble and white quartz were employed. Seven experiments are recorded, in all of which the product was well melted after an hour's blast. Both externally and on the fractured surface there were undoubted signs of crystallization. The fracture was alternately crystalline, splintery, or glassy. The thin edges of pieces were slightly transparent. The colour was more or

[4] Journ. für Techn. u. ökonom. Chemie. Erdmann. B. 10. 1831, p. 145. Extracted from the Jern-Kontorets Annaler, 1828.

less blue-grey, occasionally passing into sea-green. In most cases the product resembled the common blue agates of which mortars are made. They all had an iron-grey coating, which was not attacked by hydrochloric acid, and which, therefore, could not be due to iron derived from the carbon crucible. By exposure to a red heat in an open crucible this film disappeared, but it came again on remelting the slag, during which there was so little loss that $6^{grms},000$ of slag were only reduced to $5^{grms},997$. The average specific gravity of the product obtained in five experiments was 2·861, the extremes being 2·781 and 2·893.

CaO, SiO^3. No. 27.—This silicate generally melts far more easily than the last, so that if both are placed in the furnace at the same time it will be perfectly melted when the other is only just fritted. The two silicates so closely resemble each other that they cannot be distinguished in external appearance. This silicate seems to be somewhat more brittle than the last. The results of five experiments are recorded, and the average specific gravity of the products obtained was 2·744, the extremes being 2·731 and 2·755.

$3CaO, SiO^3$. No. 25.—The mixture could not be melted. An experiment was then made to ascertain whether the silicate $3CaO, 2SiO^3$ (No. 26) could be made to combine with more lime. Pieces of this silicate were placed in carbonate of lime and exposed to as much heat as the crucible could support. On opening the crucible the whole mass appeared to be sintered together, but on taking it out it immediately fell to pieces: only the internal part where the silicate lay remained entire, the other part of the mass being in the state of white powder. The solid nucleus remained in a coherent state during 24 hours, but it became disintegrated when moistened with water, and sometimes with the evolution of heat. Other experiments were next made by heating the silicate with less lime, and in one case the product was actually melted; but when it was taken hot out of the furnace it fell to pieces in less than a minute. By allowing the mass to cool in the crucible it remained in a coherent state during several days. This slag was analysed and found to consist of 41·10 per cent. of silica and 58·77 of lime. It might, consequently, be regarded as a mixture of two silicates of the respective formulæ $3CaO, 2SiO^3$ and $3CaO, SiO^3$. Sesquibasic silicate of protoxide of iron ($3FeO, 2SiO^3$) was mixed with sufficient caustic lime to form the silicate of lime, $3CaO, SiO^3$, after reduction of the protoxide of iron. After an hour's firing was produced a tender mass of a gray spongy glass, which dissolved in hydrochloric acid with the evolution of hydrogen—but not of carbonic acid—and the separation of gelatinous silica. Distinct metallic particles were not perceived until after repeated melting of the mass at a still higher temperature. The proportion of silica was next increased, so that equal parts of the silicates $3CaO, SiO^3$ and $3CaO, 2SiO^3$ might be formed. After an hour and a half's firing a little finely foliated cast-iron and a well-melted slag were obtained, but the latter immediately fell to powder. The last experiment was repeated with a sustained blast during two hours. A button of grey fine-grained, cast-iron was

produced and a well-melted glassy slag, which no longer crumbled to powder.

$3CaO, 4SiO^3$. No. 28.—The mixture became fluid in a certain degree and appeared to separate into two layers, of which the lower one was darker and more compact, and resembled CaO, SiO^3, while the upper one, on the contrary, had a light and spongy aspect. The lower layer was found to be composed of 64·97 of silica and 35·52 of lime.

$CaO, 2SiO^3$.—This silicate does not occur in the table. A melted mass was obtained, which, nevertheless, appeared to be homogeneous, especially when cut. Its colour was pearl-grey, passing into blue.

$3MgO, SiO^3$. No. 30.—The product was a milk-white, glassy, porous mass.

$3MgO, 2SiO^3$. No. 31.—The product was a well-melted, pearl-coloured, almost white enamel, which was crystalline externally. It seemed to melt more readily than Nos. 30 and 32.

MgO, SiO^3. No. 32.—Product similar to No. 31; more crystalline, but not so well melted.

$3CaO, 3MgO, 2SiO^3$. No. 46.—This was prepared by heating a mixture of $3CaO, 2SiO^3$ and magnesia. The product was a well-melted light blue-green glass having a granular fracture.

$3CaO, 3MgO, 4SiO^3$. No. 47.—Product a well-melted glassy slag, translucent like opal; in some places crystalline.

$CaO, 2MgO, 2SiO^3$. No. 48.—Product a well-melted partially-crystallized enamel.

$2CaO, MgO, 2SiO^3$. No. 49.—Product a well-melted opalescent glass having a granular fracture.

$CaO, MgO, 2SiO^3$. No. 51.—Product a pearl-coloured enamel, which appeared to be easily fusible.[5]

$3CaO, 2Al^2O^3, 3SiO^3$. No. 58.—Product a well-melted green glass. Its specific gravity in one experiment was 2·67 and in another 2·77.

$3CaO, 2Al^2O^3, 4SiO^3$. — Not in the table. This mixture melted readily into a sooty glass, which was dichroic. Before the blowpipe it swelled up into white froth. Two experiments were made; in one the specific gravity of the product was 2·65 and in the other 2·79.

$3CaO, 2Al^2O^3, 6SiO^3$.—Not in the table. Product similar to the last, but somewhat difficult to melt before the blowpipe. Its specific gravity was 2·56.

$3CaO, Al^2O^3, 4SiO^3$. No. 56.—Product a blue-green well-melted glass, of which the specific gravity was 2·55. In another experiment, in which the blast was scarcely continued half an hour, the product was also melted, but it was porous.

$3MgO, Al^2O^3, 2\ SiO^3$. No. 66.—Product well melted after an hour's blast. In fracture it resembled compact dichroite.

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[5] In Erdmann's Journal the formula $SC^3 + MS^3$ is given, and the same appears in the Jern-Kontorets Annaler (1828, p. 187). It appears to be a misprint for the one which I have introduced, as in every other case the silica (S) is placed *after*, and *not before*, the base.

The green and blue colours of some of the foregoing compounds were probably due to the presence of oxide of iron.

On the fusibility of certain compounds not containing silica; aluminates, &c.—That alumina may act the part of acid as well as that of base is proved by the composition of the minerals termed spinels, which occur well crystallized, and consist exclusively of alumina and a base of the RO type combined in definite atomic proportions. Beautifully crystallized compounds of this kind have been artificially prepared by Ebelmen. On the other hand, in various minerals, such as staurolite, cyanite, and kaolinite, alumina must be regarded as acting the part of base, silica being the acid. But in many silicates containing both alumina and bases of the RO type the function of alumina cannot, in the present state of our knowledge, be determined with certainty. From the foregoing experiments it appears, that when a mixture consisting of silicate of lime of the formula $3CaO, 2SiO^3$ and sufficient lime to form the silicate of the formula $3CaO, SiO^3$ is exposed to a very high temperature, a fritted mass may be produced; but this mass becomes speedily disintegrated, and much of the lime remains in a caustic state, as though it had only been mechanically diffused through the silicate. Now Sefström found that when alumina was added to this mixture of silicate of lime and lime in the proportion requisite to form an aluminate of the formula $3CaO, 2Al^2O^3$—that is, a mixture represented by the formula $3CaO, 2SiO^3+3CaO, 2Al^2O^3$—the effect of heat was quite different. A well-melted mass was then obtained, of which the surface was rendered uneven by fine acicular crystals. At the upper part it was blue-grey, but underneath, where it was in contact with the charcoal, it had the lustre of iron, which is often produced in slags by the presence of the smallest amount of iron in the reagents employed. In the colour and appearance of the fracture it resembled phosphate of lime; its specific gravity was 2·888. The following experiments were made by Sefström on the formation of aluminates of lime in the furnace.

$3CaO, 2Al^2O^3$.—From a mixture composed according to this formula a porous dirty-yellow coloured slag was obtained. In another trial the product was compact, black, and of the specific gravity 2·76. When heated before the blowpipe it became yellow, and then exactly resembled yellow wax. In a third experiment, after an hour's blast, a product similar to the last was obtained. Of all the aluminates which Sefström prepared this was the most fusible.

CaO, Al^2O^3.—Two experiments gave the same results. The product was a melted compact mass, of which, internally, the colour was between grey, yellow, and brown; in fracture it had a waxy lustre; it contained small white particles of unfused matter.

$3CaO, Al^2O^3$.—The product was a melted, glassy, yellowish-green slag.[6] Before the blowpipe it was light grey and infusible. This aluminate had the same remarkable property as the corresponding

[6] Von einer Mittelfarbe zwischen isabellgelb und grasgrün.

silicate, namely, that of falling to fine powder after a time. However, in the case of the aluminate this did not occur until after some months.

Sesquioxide of iron and lime.—I find that a mixture of these substances in certain proportions yields a well-melted slag. A mixture consisting of 160 grains of pure sesquioxide of iron and 100 of white marble (= 56 grains of lime)—that is, in the ratio of Fe^2O^3 : CaO—was exposed in a covered clay crucible to a high temperature. It was perfectly melted, and when broken across resembled a black, opaque, vitreous slag: the crucible had one large perforation. In a second experiment a mixture, according to the same formula, of 40 grains of sesquioxide of iron and 25 of carbonate of lime was heated in a clay crucible lined with platinum foil. It was perfectly melted and escaped through the crucible.

Berthier experimented upon the following mixtures:—

	Alumina.	Lime.	Magnesia.
1. 6CaO, 3MgO, Al^2O^3	19·9	56·5	23·6
2. 3CaO, 3MgO, Al^2O^3	27·5	39·3	33·2
3. 6CaO, 3MgO, $4Al^2O^3$	49·9	35·3	14·8
4. 4CaO, 3MgO, $3Al^2O^3$	47·0	33·8	19·2
5. CaO, MgO, Al^2O^3	53·5	25·5	21·0

1. (S.) Product granular, dull, fissured, very light, gritty between the fingers. It had a little diminished in volume.

2. (S.) Product granular, dull, sufficiently coherent, but gritty under the finger-nail. Considerably contracted.

3. (G. f.) Button well melted, bubbly, pale olive green, strongly translucent, fracture oven, shining, and waxy, presenting no sign of crystallization.

4. (G. f.) Button well rounded, compact, stony; fracture uneven, slightly shining, transparent in some parts.

5. (S.) Product granular and porous; the interior of the pores rounded, which proves that softening had occurred.

On fluor-spar as a flux.—Fluor-spar occurs not unfrequently in ores. Its formula is CaF; its composition is—

	Per cent.
Calcium, 1 equiv. = 20	51·54
Fluor ... 1 equiv. = 18·8	48·45

At 60° p. it neither melts nor softens, but contracts much. At a higher temperature it melts sufficiently easily into a transparent liquid, which crystallizes on cooling. Heated in the porcelain-furnace at Sèvres in a brasqued crucible it produced a compact mass, free from bubbles, and of a crystalline structure. The grains were very small, but transparent and well defined, and under the microscope their form could be recognised.[7] The letter B will be attached to those of the following experiments which were made by Berthier.

	1. grammes.	2. grammes.
Fluor-spar	100	100
Quartz in powder	30	47

[7] Berthier, Tr. des Essais, 1, p. 480.

1 B. (S.) Button perfectly rounded, compact, without the slightest bubble; fracture even, finely granular, and crystalline, resembling white statuary marble. It weighed 114 grms., so that there was a loss of 16 grms. The edges of the crucible were lined—especially towards the angles—with bubbly, colourless, and transparent glass, arising, according to Berthier, from the action of fluoride of silicon evolved upon the substance of the crucible. This gas, Berthier states, was produced by the action of the gases containing hydrogen which were present in the furnace.

2 B. (G. f.) Button compact, free from bubbles, white, opaque, very hard; fracture stony, uneven, resembling compact quartz. It weighed 126 grms., so that there had been a loss of 21 grms. The edges of the crucible were coated with glass.

	3.	
	grammes.	per cent.
Fluor-spar	100	30·3
Quartz in powder	190	57·5
Alumina	40	12·2

3 B. (S.) Heated in a brasqued crucible. Button well rounded, compact, without the least bubble; fracture partly lamellar, partly conchoidal, translucent, clear grey. It weighed 270 grms., so that the loss amounted to 60 grms.

	4.
	grammes.
Fluor-spar	100
Quartz in powder	130
Kaolin washed and calcined	100

4 B. Heated in a brasqued crucible (G. f.) Button well melted, compact, translucent, white; fracture uneven, very hard. It weighed 287·5 grms., so that the loss amounted to 42·5 grms.

Berthier remarks that fluor-spar acts as a flux in two ways: by combining directly with silicates and forming fusible compounds; but chiefly by acting upon silicates and causing an evolution of fluoride of silicon. Fluor and silicon are thus removed, and the lime is proportionately increased. The agency of gases containing hydrogen does not seem to be necessary to determine the reaction, for the calcium may be oxidized at the expense of the oxygen of the silica, and the silicon, reduced, escape in combination with fluor.

Fluoride of calcium does not appear to form fusible combinations with oxides. B.

	5.		6.	7.
	a.	*b.*		
	grains.	grammes.	grammes.	grains.
Fluor-spar	1 equiv. 195	9·87	2 equiv. 19·74	1 equiv. 97·5
Sulphate of baryta	1 equiv. 585	29·16	1 equiv. 29·16	2 equiv. 585

5*a*. By Smith in my laboratory. Fused at a bright red heat, but not very liquid. Product hard, brittle; fracture indistinctly crystalline. There was a cavity in the centre lined with indistinct crystals; it had a pink greyish-white colour, due, probably, to the fluor-spar.

5*b*. B. Although heated very strongly it did not become perfectly

liquid. Product puffed out in some parts; fracture granular crystalline. The sides of the cavities were polyhedral, and some small prismatic crystals might be perceived here and there.

6. B. Strongly heated; completely melted. Compact; fracture slightly crystalline, a little translucent, colourless, no indication of crystals.

7. By Smith. Does not melt so easily as No. 5. Product hard, brittle; fracture compact, with traces of indistinct crystalline plates; colour pink greyish-white.

	7.	8.	
		a.	*b.*
	grammes.	grains.	grammes.
Fluor-spar, ...	2 eq. 19·74 ...	... 1 eq. 390	... 1 eq. 9·87
Sulphate of lime,	1 eq. 21·64 (cryst.)...	1 eq. 680 (dry)	... 1 eq. 21·64 (cryst.)

	9.		10.
	a.	*b.*	
	grains.	grammes.	grammes.
Fluor-spar, ...	1 eq. 195	4·93	1 eq. 2·47
Sulphate of lime,	2 eq. 680 (dry) ...	21·64 (cryst.) ...	4 eq. 21·64 (cryst.)

7. B. Melted at a rather strong heat. Product compact; fracture uneven, with only faint traces of crystallization.

8*a*. By Smith. This mixture melts at a lower temperature than that with sulphate of baryta, and becomes very liquid. Product hard, fragile, opaque, pinkish-white; fracture fibrous in the outer portion, but the centre part consists of shining indistinct crystalline plates. *b*. B. Very quickly and completely melts and becomes extremely liquid. Product crystalline, consisting of large plates crossing each other in different directions; translucent, white, slightly pearly; it contained cavities in which were determinable crystals. It is the most fusible compound of fluor-spar and sulphate of lime.

9*a*. By Smith. Result similar to 8*a*, but the crystallization was more distinct. *b*. B. Becomes very liquid. Product compact, free from bubbles, white, slightly translucent; fracture granular, in plates, very brilliant.

10. B. Although heated very strongly, it did not completely melt, but was only softened. Product very bubbly, opaque, white; fracture finely granular; the internal surfaces of the cavities polyhedral.

	11.	12.
	grammes.	grammes.
Fluor-spar.....	1 eq. 19·74	2 eq..... 19·74
Anhydrous sulphate of soda,	1 eq. 35·68	1 eq..... 17·84

11 B. Melted and became as liquid as water. Product contracted very much on cooling; compact; fracture granular, crystalline, and strongly translucent, but there were no isolated crystals.

12 B. Melted with a slight bubbling, but it became extremely liquid. Product resembled No. 11, but was harder and more tenacious.

	13.	14.
		grammes.
Fluor-spar.....	equal weights.	4 eq..... 19·74
Bone-ash.....		1 eq..... 27·67

13. By Smith. This mixture fuses at a red heat. Product compact, hard, brittle, opaque, white; fracture slightly conchoidal. The central part consisted of small, interlacing, acicular crystals.

14. B. Contracted, so as no longer to touch the sides of the crucible; softened, but without melting. Product very coherent; bubbly, especially on the lower part; fracture dull and stony.

According to Berthier fluor-spar has no action on sulphides; when melted with them there is usually only simple mixture, but when the sulphide is very fusible and heavy it separates and subsides to the bottom of the crucible.

'Plattner's experiments on the melting-points of slags.—In these experiments Plattner endeavoured to determine the precise thermometric melting-points of various silicates occurring in slags, and to this end he availed himself of the method proposed and employed by Prinsep for the measurement of high temperatures.[8] This method consists in the application of what Prinsep terms *pyrometric alloys* of gold and platinum. From the fusion of pure gold to that of pure platinum he assumed 100 degrees, adding one per cent. of the latter metal to the alloy which measured each successive degree. The melting-point of gold is the zero of this scale. Prinsep did not suppose that these hypothetical degrees represented equal increments of heat throughout the scale, but, as he observes, they always indicate the same intensity. The alloys are rolled out and cut into pieces of the size of a pin's head; eight or ten of these alloys are placed at a time in a small *pyrometer cupel*, each in a separate cavity, as shown in the annexed woodcut (*a*). In three of these cavities the metal is shown melted. The cupel is provided with a nicely fitting lid (*b*). Now, as Prinsep observes, when a series of such alloys has once been prepared, the heat of any furnace may be expressed by the alloy of least fusibility which it is capable of melting; but Plattner has attempted to assign precise temperatures in Centigrade degrees to the melting-points of these alloys. He adopted the principle of a process which had been previously employed by B. de Saussure in the estimation of high temperatures.[9] The process consists in determining the greatest amount of any substance which can be melted before the blowpipe and comparing the diameter of the bead with that of the greatest amount of silver which can also be melted in the same manner. Daniell, by means of his platinum pyrometer, found the melting-points of silver and gold to be respectively 1023° C. and 1102° C.; and, accepting these as correct, Plattner proceeded to deduce the melting-point of platinum. He *assumed* that the melting-point of alloys of silver and platinum would be the mean of

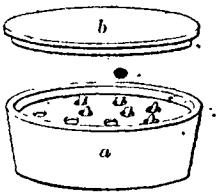

Fig. 1.

[8] Phil. Trans. part 1, p. 79. 1828.

[9] Die Anwendung der erwärmten Gebläseluft im Gebiete der Metallurgie, F. Th. Merbach, 1848, p. 288 et seq. Plattner's experiments are recorded in extenso in this work, from which I have derived my knowledge of his results.

those of the two metals. He found by experiment that an alloy composed of 9·5 per cent. of platinum and 90·5 of silver had the same melting-point as gold.

Let x be the melting-point of platinum.

$$\frac{9{\cdot}5x + 90{\cdot}5 \times 1023}{100} = 1102\,; \quad x = 1855^{\circ}$$

in round numbers. He next ascertained the maximum amount of gold which could be melted in a given time by a given blowpipe flame produced by a blast of constant but very slight pressure. The fusion was effected in small clay crucibles of the same shape and size ($\frac{1}{2}$ in. high and $\frac{1}{4}$ in. in diameter at the top, Prussian measure). In order that the heat might be uniformly applied, each crucible was placed in a cavity in the end of a piece of good soft charcoal about four inches long and one inch square. The maximum amount of gold thus melted was 2290 millegrammes and 1990 millegrammes of an alloy composed of 1760 of gold and 230 of platinum. When more gold, or ever so small a quantity of platinum, was added the fusion was rendered imperfect. Now in the case of the gold the number of degrees of heat may be estimated as 2290×1102 (the melting-point of gold), but in the case of the alloy the number of degrees represented by the fusion of the gold is 1760×1102. It is inferred that the number of degrees required for the fusion of 230 of platinum is equal to that required for 530 of gold, that is, the difference of the weight of gold fused in the two cases. Hence the melting-point of platinum should be $\frac{530 \times 1102}{230} = 2539^{\circ}$. In a similar manner Plattner ascertained that 100 millegrammes of an alloy composed of 70 of gold and 30 of platinum could be melted under the same conditions and in the same time as 100 millegrammes of cast-iron, of which the melting-point, according to Daniell, is 1530° C. From these latter data the number 2534° C. was deduced as the melting-point of platinum.

Objections to the method.—This method of estimating high temperatures involves an assumption that the melting-point of alloys is the mean of the melting-points of their component metals, and this assumption, as will hereafter be shown, is entirely opposed to numerous well ascertained facts. Besides, it is obvious that, notwithstanding all the precautions which appear to have been taken by Plattner in conducting his experiments, it must be extremely difficult, not to say impossible, to ensure the necessary identity of conditions in successive experiments, and to determine the exact moment at which perfect fusion is effected. The result of the experiment with cast-iron, irrespective of the objections just stated, must be regarded as worthless, because, under the term cast-iron, may be comprised varieties of metal which widely differ, both in chemical composition and physical characters. Although we may not admit the correctness of the principle of Plattner's measurement of high temperatures, yet we may accept his experimental results as affording practical information of value. The melting-points

of metals and their alloys are fixed and unvarying, except under extraordinary conditions of great pressure; and, as they extend through a very wide range of temperature, they may be conveniently employed in the determination and comparison of high temperatures.

Melting-points of silicates as indicated by the fusion of alloys of gold and platinum.—It is stated that the fusion of a silicate may be effected at a *lower* temperature than that of the *simple mixture* of its components; but I doubt whether this statement has been satisfactorily proved. That a longer time may be necessary to effect the fusion at a given temperature in the latter case than in the former must be admitted, but it is probable that fusion would be equally well effected in both cases at the same temperature provided sufficient time be allowed. Plattner made numerous experiments to ascertain the melting-points of various silicates as indicated by the fusion of alloys of gold and platinum, and for this purpose he employed a pyrometer cupel made of well-burnt fireclay and an air-furnace. He also effected the fusion of these silicates before the oxyhydrogen blowpipe. Nos. 15, 16, 26, 27, 31, 32, 42, 44, in the table of Berthier's results, were melted at the same temperature as an alloy consisting of 42 per cent. of gold and 58 of platinum; Nos. 35, 36, at the same temperature as an alloy of 41 gold and 59 platinum; Nos. 47 and 56 at the same temperatures respectively as alloys of 45 gold and 55 platinum, and 43 gold and 57 platinum; and Nos. 69, 70, at the same temperatures respectively as alloys of 52 gold and 48 platinum, and 49 gold and 51 platinum. Other results obtained by Plattner are recorded in the following table.

	1.	2.	3.	4.	5.	6.
Silica	50·0	58·0	48·0	50·0	36·5	32·7
Alumina	17·0	6·0	9·0	16·0	8·5	7·0
Baryta	..	..	..	1·5	..	..
Lime	30·0	22·0	4·5	3·0	4·0	..
Magnesia	..	10·0	1·5	1·5	3·0	..
Protoxide of iron	3·0	2·0	37·0	38·0	40·5	60·3
Protoxide of manganese	..	2·0	..	..	..	..
Protoxide of lead	..	..	..	..	7·5	..

Temperature at which the silicate was formed, as indicated by the melting-points of alloys of gold and platinum.

	Au. Pl.	Au. Pl.	Au. Pl.	Au. Pl.	Au. Pl.	Au. Pl.
In a carbon crucible	46+54	46+54	..	..	..	..
In an iron crucible	..	..	59+41	56+44	75+25	67+23
In a clay crucible	..	..	60+40	57+43	76+24	75+25

Temperature at which the silicate melts after its formation, as indicated by the melting-points of gold and platinum.

	Au. Pl.	Au. Pl.	Au. Pl.	Au. Pl.	Au. Pl.	Au. Pl.
In a carbon crucible	77+23	76+24	..	..	..	..
In an iron crucible	..	..	84+16	82+18	85+15	83+17
In a clay crucible	..	..	84+16	82+18	85+15	84+16

Supposed sulphosilicates.—Plattner heated a mixture of 29·1 parts of silica and 108·0 of sulphate of baryta (heavy spar) in a carbon crucible. In this mixture the ratio between the silica and baryta is the same as in the silicate of the formula $3BaO, 2SiO^3$. The product was a greyish-yellow, compact, melted mass, of which the fracture was uneven, apparently crystalline, but without lustre. Its surface was polyhedral, iron-black (probably due to carbon), and of a semi-metallic lustre. It evolved a strong hepatic odour. When the powdered mass was treated with water sulphuretted hydrogen was liberated, and a small quantity of sulphide of barium was dissolved; and when acted upon by hydrochloric acid it was only very imperfectly decomposed with the evolution of the same gas. This melted product was produced at a far lower temperature than that required for the formation of the corresponding silicate of baryta, and Plattner inferred that it consisted of a combination of silica with oxysulphide of barium. A similar experiment was made with sulphate of lime (calcined gypsum). The silica and lime were in the proportion necessary to form the silicate of the formula CaO, SiO^3; the mixture was exposed in a carbon crucible to a temperature corresponding to the melting-point of an alloy of 42 gold and 58 platinum. The product was not melted, but consisted of a greyish-white, easily-pulverizable, sintered mass, which evolved a tolerably strong hepatic smell. In neither of these experiments was the product analysed, and, consequently, there is no certain evidence to prove the precise nature of the reactions and to justify a belief in the existence of sulpho-silicates. Sulphate of baryta is so easily reduced at a low temperature that Mr. Sewell of Nottingham, many years ago, obtained a patent for the production of carbonic acid by heating a mixture of sulphate of baryta and carbon in a common gas-retort. I visited Mr. Sewell's works and saw the process in operation. As in Plattner's experiments carbon crucibles were employed, the formation of sulphides is readily explained, and the temperature at which their formation would occur is without doubt much below what would be necessary to effect the combination of silica with either lime or baryta. Le Play[1] admits the existence of a sulpho-silicate of iron, but, as it appears to me, on insufficient chemical evidence.

[1] Description des Procédés Métallurg. etc. p. 212.

FUEL.

THE term is used to denote substances which may be more or less completely oxidized or burned by means of atmospheric air, and evolve heat capable of being applied to economical purposes. There are only two elements which are thus applied, namely, carbon and hydrogen. All fuel consists either of vegetable matter or of the products of the decomposition of that matter naturally occurring or artificially induced. Vegetable matter, which chiefly consists of woody tissue, may *practically* be regarded as composed of carbon, hydrogen, and oxygen, together with a small quantity of so-called earthy matters. The former constitute the *organic* part, and the latter the *inorganic* part of vegetable matter. The original source of the organic part is water and the carbonic acid of the atmosphere, both of which are decomposed in the economy of plants through the agency of solar light. The sun, therefore, is really the source of the heat-producing power of all fuel.

From the preceding considerations it will appear that the hydrogen employed as fuel must always be in association with carbon; but the converse is not true, for carbon, which may be regarded as *practically* free from hydrogen, may be procured abundantly and employed as fuel. Thus the combustible part of anthracite and well-burnt charcoal or coke consists essentially of carbon with a small proportion of hydrogen, which may be practically neglected. In all fuel containing carbon, hydrogen, and oxygen, the proportion of hydrogen may be equal to, or greater, but *never less* than, that required to form water with the oxygen. It may be shown that it is only the hydrogen in *excess* which is available as a source of heat, so that in the combustion of a substance of which the composition may be represented by carbon and water, the carbon alone is the source of heat. The hydrogen, indeed, in this case causes a loss of a large amount of otherwise *available* heat, in as much as it may be regarded as virtually existing in combination with oxygen in the state of water, and the carbon cannot be burned without the evaporation of this water at the expense of the heat developed by its combustion. It is true that the hydrogen may perform an important function in such a fuel in generating *flame*, but the proposition is, nevertheless, true that it not only does not contribute to the *actual amount* of heat produced, but consumes, so to speak, no inconsiderable portion of it.

The products of the perfect oxidation or combustion of carbon and hydrogen are carbonic acid and water respectively. Both products are obtained on the perfect combustion of any compound of carbon and hydrogen, or of these elements associated with oxygen. The amount of heat which any element in the same allotropic condition

developes on complete combustion is perfectly definite, and is the same whether combustion be *slowly* or *rapidly* effected; it is as definite as the amount of electricity evolved in the voltaic battery by the oxidation of a metal like zinc, for example. It has been ascertained that the amount of heat produced by the complete combustion of carbon and sulphur varies in a small, though very sensible, degree with their allotropic condition. The term *perfect*, or *complete*, which has been used to qualify the degree of oxidation or combustion of carbon and hydrogen, requires explanation. In respect to carbon it expresses the *maximum* of oxygen with which it is capable of combining, but in respect to hydrogen it does not, for oxygenated water, or peroxide of hydrogen, contains twice as much oxygen as water. Yet in respect to both elements it expresses the highest degree of *stability* in the product of oxidation, the affinity by which the second atom of oxygen is held in combination in oxygenated water being extremely feeble.

The *intensity*, or pyrometric degree, of heat, must not be confounded with the *quantity* of heat developed on combustion. The quantity of heat generated by the perfect combustion of a body (A) may be much greater than that of another body (B), weight for weight, but the intensity of the heat derived from B may far exceed that from A. However, the intensity of the heat developed on the combustion of the *same* body will, *cæteris paribus*, be proportionate to the *rapidity* of combustion; or, in other words, it will be inversely as the time in which combustion is effected. The term *calorific intensity* will be employed in contradistinction to *calorific power*, which expresses the relative quantity of heat.

When a piece of well-burnt dry charcoal is ignited and exposed freely to the air, it burns without any sensible flame, and the product is carbonic acid. When, on the other hand, a piece of light dry wood is ignited, it burns with much flame, and the products, if the combustion is perfect, are carbonic acid and water. Ordinary flame is gas or vapour of which the *surface*, in contact with atmospheric air, is burning with the emission of sensible light. The truth of this proposition may be easily demonstrated by experiment upon the flame of a candle or gas-jet, as is stated in every treatise on chemistry. Indeed, if it were not so, the gas and its supporter of combustion must be mixed; but in that case there would be an explosion, attended only with the instantaneous production of flame. The piece of charcoal contains nothing from which any sensible amount of inflammable gas can be produced by the application of heat, and the solid carbon, in ignition, passes directly to the state of carbonic acid. Hence there can be no flame. But when a piece of wood is ignited, the case is altogether different. The inner substance of the wood in contact with its burning surface is precisely in the condition of wood which is heated in a close vessel and evolves various combustible gaseous and liquid volatile products. Hence there must be flame. However numerous these products may be, it should be remembered that, so long as they are ultimately converted into carbonic

acid and water, the proposition previously announced is correct in respect to the quantity of heat developed. When a piece of charcoal smoulders away in atmospheric air, or when it is burned in oxygen gas, light is evolved. In the former case it is only a dull red light, but in the latter it is intensely brilliant, yet there is no sensible flame. This statement must be made with a certain degree of reservation. It is customary to refer the production of flame to the so-called combustible gases; but it would be equally correct to refer it to the so-called supporter of combustion.

The luminosity of flame is caused by the presence of particles of *solid* matter within, or in immediate contact with, the gas in active combustion. In the flame of a candle or jet of coal-gas this matter is carbon in a fine state of division, the existence of which may be shown by holding a cold glass rod for a second or two across the flame, when the portion within the burning surface will be covered with a black soot-like deposit. The flame of a candle or of gas burning in atmospheric air is highly luminous, whereas that developed by the combustion of hydrogen by oxygen is very feebly so; yet the intensity of the heat of the former is very small as compared with that of the latter. The luminosity, therefore, of flame affords no certain indication of its temperature. When the flame resulting from the combustion of hydrogen and oxygen in admixture, in the proportion in which they exist in water, is projected upon a piece of lime, or some other substance, an intensely brilliant light is produced, and, under these conditions, there is a correspondence between the light and heat of flame in respect to intensity.

As the temperature of a gas in active combustion under ordinary circumstances is much higher—and its specific gravity, consequently, much lower—than that of the surrounding atmosphere, flame will necessarily tend to rise. The length of flame will depend on the rapidity with which the combustible gas is generated, and the velocity with which flame rises will be proportionate, *cæteris paribus*, to the difference of temperature between the gas in combustion and the surrounding atmosphere.

It has been stated that when a *piece* of charcoal is ignited and exposed to the atmosphere it burns without flame, but the result may be different when charcoal is burned in *mass*, as in a furnace. In this case flame may be copiously produced by the combustion of carbonic oxide, which is generated when carbonic acid comes in contact with charcoal heated to bright redness; and this condition always occurs in a furnace of which the fire-place contains charcoal to the depth of a few inches. When atmospheric air impinges upon incandescent charcoal carbonic acid is formed, but as this gas rises through the superincumbent mass of charcoal heated to bright redness, it is converted, more or less perfectly, into carbonic oxide, which, afterwards coming in contact with atmospheric air, burns with its beautiful and characteristic blue flame.

ON THE CALORIFIC POWER OF FUEL.

Although there is no means of estimating the *absolute* amount of heat evolved by the combustion of a body, yet the *relative* amounts of heat evolved by the combustion of different bodies may be accurately determined. Rumford estimated the calorific power of a body by the number of parts by weight of water which one part by weight of the body would, on perfect combustion, raise one degree in temperature. Thus 1 part by weight of charcoal in combining with $2\frac{2}{3}$ of oxygen to form carbonic acid will evolve heat sufficient to raise the temperature of about 8000 parts by weight of water 1° C. Similarly, 1 part by weight of hydrogen in combining with 8 parts by weight of oxygen to form water will raise 34000 parts by weight of water 1° C. The relative calorific powers, therefore, of carbon and hydrogen are as 8 : 34.

The amount of heat required to raise 1 gramme (15·432 grains) of water from 0° to 1° C. is conventionally taken as the *unit of heat* or *calorie* of the French.[3] It is not a matter of indifference whether any portion of the thermometric scale be selected, because a greater amount of heat is necessary to increase the temperature of water by 1° near the boiling-point than at lower temperatures.

Rumford employed in his experiments a rectangular vessel of thin sheet-copper containing a worm of three horizontal coils of the same metal. The vessel was 8 inches long, $4\frac{1}{4}$ broad, and $4\frac{1}{4}$ deep. The worm consisted of a flat tube $\frac{1}{2}$ inch in depth and 1 in breadth. One end protruded through the top of the box and the other was fitted to a circular hole in the bottom, 1 inch in diameter, and in this hole was inserted a funnel, of which the mouth was $1\frac{1}{4}$ inch wide. The lower end of the worm was situated near one of the short sides of the vessel, and the other end issued vertically near the opposite side. A tube was inserted in the top of the box, through which could be introduced a thermometer, having a cylindrical reservoir in length equal to the depth of the vessel, so that by this means the mean temperature of the water with which it was filled could be ascertained. The substance of which the calorific value was required was burned under and within the funnel-mouthpiece, when a current of air would circulate upwards through the worm and escape at the opposite end. The heated gaseous products of combustion would thus convey the heat developed through the worm, from which it would be communicated to the surrounding water. In order to counteract the error arising from loss by radiation the temperature of the water with which the vessel was filled was reduced, just before the commencement of an experiment, a few degrees—say 5—*below* that of the surrounding atmosphere, and the

[3] As English writers on this subject usually employ the French gramme for the unit of weight, I have followed their example. It is quite immaterial what unit is selected. The reader may substitute *parts by weight*, the *English grain* or *pound* for gramme.

combustion was continued until the temperature of the water was exactly 5 degrees *above* that of the surrounding atmosphere. By this arrangement it was estimated that the vessel would receive as much heat by radiation and conduction as it would lose during the experiment. With a view to diminish the effect of conduction as much as practicable the vessel was supported on pillars of wood. In order to test the power of the instrument to extract the whole of the heat from the gaseous products of combustion, they were made to traverse a second vessel, similar in all respects to the first, when it was found that the temperature of the water in the second vessel was not increased.[9]

The data required in the use of this instrument, or *calorimeter*, are as follow:—

The weight of the substance consumed (n).
The weight of the water (w).
The weight of the copper (c) and the specific heat of copper (s).
The initial temperature of the water, or that at the beginning of an experiment (t).
The final temperature of the water, or that at the close of an experiment (t').

Other corrections for the glass of the thermometer, &c., would be necessary in experiments of great precision, but in Rumford's apparatus, which is comparatively rude, they would be superfluous.

By multiplying the weight of the copper used in the instrument by the specific heat of copper the weight of water is found, which, in respect to absorption of heat, would be exactly equivalent to the weight of copper in the instrument.

Let x represent the amount of heat produced by the combustion of 1 part by weight of any given body in atmospheric air; the following formula will then express the calorific power of the body.

$$nx = (t' - t)(w + cs)$$
$$\therefore x = \frac{(t' - t)(w + cs)}{n}$$

For example—

Let n = 10 parts by weight.
w = 8900 ditto.
c = 1000 ditto.
s = 0·09515 (Regnault).
t = 11° C.
t' = 20° C

Then—

$$x = \frac{(20 - 11) \cdot (8900 + 1000 \times 0{\cdot}09515)}{10} = 8095$$

That is to say, 1 part by weight of the substance on perfect combustion in atmospheric air raises 8095 parts by weight of water 1° C., or in round numbers 8000 times its weight. This is nearly the calorific power of charcoal.

[9] Vide Encyclop. Metropolitana, 1830. Mixed Sciences, v. 2, p. 266.

The calorific power of various bodies has been investigated by Lavoisier, Dulong, Despretz, and Grassi; but we are indebted to Favre and Silbermann,[1] and to Andrews,[2] for the most recent researches on the subject. The apparatus employed in these researches was founded on the same principle as that of Rumford's, but constructed so as to ensure far more accurate results. All necessary corrections in the calculations have been made, and every precaution seems to have been taken in conducting the experiments; and, in general, the results of these later observers are in close accord.

Researches of Favre and Silbermann.

Calorific power of carbon.—Favre and Silbermann experimented on carbon in the different allotropic states of diamond, graphite, and charcoal. Andrews and they ascribe the discrepancy in the results of previous observers to the ignorance of the fact first announced by Dumas and Stas that, during the combustion of carbon, even in oxygen gas, a certain amount of *carbonic oxide* is always produced. And when carbon is only oxidized to the degree of carbonic oxide, *much less* heat is evolved than when it is oxidized to the maximum, so as to form carbonic acid. As it was not found possible to prevent the formation of some carbonic oxide during the combustion of carbon, even under the most favourable conditions, the amount of carbonic oxide produced in each experiment was accurately determined. This was done by passing the products of combustion first through a solution of potass, which absorbed the carbonic acid, and afterwards through a tube containing incandescent protoxide of copper. By this means the carbonic oxide was completely converted into carbonic acid, which was collected by a solution of potass and weighed. The total amount of carbon consumed may thus be found, as well as the relation between the carbonic acid and carbonic oxide produced.

Calorific power of carbonic oxide.—To effect the perfect combustion of carbonic oxide it was found necessary to adopt the plan of Dulong, and burn it in admixture with one-third of its volume of hydrogen. The relative proportion of the two gases was ascertained in each experiment by passing some of the gaseous mixture in its course to the combustion-chamber of the calorimeter over incandescent protoxide of copper, and determining the weight of the carbonic acid and water thereby produced, as in the process of an ordinary organic analysis. From the mean of two experiments, 1 gramme of carbonic oxide evolves 2402·7 (say 2403) units of heat by conversion into carbonic acid.

Calorific power of wood-charcoal.—Correction was made in the manner already described for the amount of carbonic oxide formed in each experiment. The charcoal operated on was freed from associated impurities by different methods, which all furnished a product yielding the same amount of heat on combustion, provided it was completely deprived of hydrogen. The same results were obtained when the

[1] Ann. de Ch. et de Phys., 3, s. 1852. 34, p. 357; 36, p. 5; 37, p. 406.

[2] Philos. Magazine, 1848. 32, p. 321, p. 426.

charcoal was heated to the temperature of iron-assays—or at about 1000° C. during a long time—or when heated successively at incipient redness in a current of chlorine, hydrogen, and nitrogen. After this treatment it was again calcined. Special arrangements were adopted to determine the amount of hydrogen which might be present in the charcoal, and a correction was made accordingly. From the mean of a considerable number of results, 8080 was deduced as the calorific power of carbon in the state in which it exists in purified wood-charcoal. The calorific power of carbon in other states will be found in the table below.

It has been stated that by the conversion of 1 gramme of carbonic oxide into carbonic acid, 2403 units of heat are evolved. The amount, therefore, of carbonic oxide containing 1 gramme of carbon will evolve 5607 units of heat. But 1 gramme of carbon, in passing to the state of carbonic acid, evolves 8080 units. Hence, 1 gramme of carbon, by conversion into *carbonic oxide*, will evolve (8080 – 5607 =) 2473 units. This is a very striking fact, that carbon should, on passing only to the state of carbonic oxide, evolve less than half the amount of heat which it evolves on passing to the state of carbonic acid. The probable explanation is, that when carbon combines with the first equivalent of oxygen to form carbonic oxide, much heat is rendered latent by the passage of the carbon from the solid to the gaseous state. It was formerly propounded that the heat developed in combustion is proportionate to the oxygen consumed; but in the case of carbon at least this law is assuredly erroneous.

There is no exact relation, as will appear from the following table, between the calorific power and the specific heat of carbon in different allotropic states.

	Calorific power.	Specific heat (Regnault).
Wood-charcoal	8080	0·24150
Carbon of gas-retorts	8047·3	0·20360
Artificial graphite	7762·3	0·19702
Native graphite	7796·6	0·20187
Diamond	7770·1	0·14687

A remarkable fact was observed in respect to diamond, namely, the change effected in its calorific power by heating it to 400° C. or 500° C., and then allowing it to cool before burning it. Thus, the calorific power, before the preliminary heating, was 7770·1, and, afterwards, 7878·7, the difference being 108·6.

Calorific power of hydrogen.—From the mean of six determinations, which all closely approximate, the calorific power of hydrogen was found to be 34462. The weight of hydrogen consumed in each experiment was deduced from the weight of water collected.

Calorific power of Marsh-gas (CH^2).—The gas was made by heating baryta with crystallized acetate of soda. Its calorific power by combustion in oxygen was found to be 13063, as deduced from the mean of three determinations. The relation in weight between the carbon and hydrogen in this gas is as 3 : 1. If, therefore, its calorific power were the mean of that of its elements, the number would be (8080 × 3

$+ 34462) \div 4 = 14675{\cdot}\dot{5}$. Assuming that the calorific power of the hydrogen is the same as in its uncombined state, the calorific power of carbon (x) as it exists in Marsh-gas is—

$$\frac{3x + 34462}{3 + 1} = 13063$$

$$x = 5930{\cdot}3$$

Calorific power of Olefiant gas (C^2H^2).—From the mean of two determinations the number deduced was 11857·8. The relation in weight between the carbon and hydrogen in this gas is as 6 : 1. If, therefore, its calorific power were the mean of that of its elements, the heat developed by the combustion of the carbon existing in 1 gramme of the gas would be $\frac{6 \times 8080}{6+1} = 6925{\cdot}7$; and that of the hydrogen would be $\frac{1 \times 34462}{6+1} = 4923{\cdot}1$. The sum of these numbers is 11848·8, or nearly the number found by experiment.

Favre and Silbermann make the remarkable statement that when carbon is converted into carbonic acid by oxygen, as it exists in protoxide of nitrogen, more heat is evolved than by its combustion in pure oxygen. Thus its calorific power by combustion in the former gas was found to be 11158, or 3078 in excess of 8080, its calorific power when burned in oxygen. If this be correct, and oxygen and nitrogen could be directly combined so as to form protoxide of nitrogen, cold should be produced during the combination.

Berthier's process of estimating the calorific power of Fuel.—In the erroneous belief that the amount of heat evolved by combustion is proportionate to the amount of oxygen consumed, Berthier proposed to determine the calorific power of fuel by burning it by means of the oxygen contained in protoxide of lead. When charcoal, for example, is heated in admixture with a sufficient quantity of protoxide of lead, it is converted into carbonic acid at the expense of the oxygen of the protoxide, with the reduction of an equivalent proportion of lead. In respect to pure carbon, or matters containing carbon *without any other reducing agent*, this process might be employed with advantage, as it may be easily practised, and would yield correct results in the comparison of one carbonaceous matter with another. But when hydrogen is present, as is nearly always the case in fuel—even in charcoal and coke—it may lead to erroneous conclusions, as will clearly appear from the following considerations. Three parts by weight of carbon reduce the *same* quantity of protoxide of lead as one part by weight of hydrogen. But the calorific powers of carbon and hydrogen respectively in round numbers are as 8 : 34. The calorific power, therefore, of 3 of carbon : 1 of hydrogen is as 24 : 34. Hence, the same weight of lead obtained by reduction would in the case of carbon indicate a calorific power of 24, and in that of hydrogen 34; so that the process is inapplicable to the determination of the calorific power of fuel containing variable proportions of carbon and hydrogen.

Berthier thus describes his process.[3] Mix intimately 1 part of the

[3] Traité des Essais, 1, 228.

TABLE OF CALORIFIC POWERS.

One gramme of each Substance.	Supporter of Combustion.	Product of Combustion.	Number of Grammes of water heated 1°C.	Name of observer.
Diamond	Oxygen..	Carbonic acid ...	7770	Favre and Silbermann.
Graphite, native	,,	,,	7811·5	,,
,, ,, another specimen	,,	,,	7781·7	,,
,, artificial from blast-furnaces	,,	,,	7787·5	,,
,, ,, another specimen	,,	,,	7737·1	,,
Carbon of coal-gas retorts ...	,,	,,	8047·3	,,
Charcoal from wood	,,	,,	7237	,,
,, ,,	,,	,,	7167	Lavoisier.
,, ,,	,,	,,	7912	Dulong.
,, ,,	,,	,,	7714	Despretz.
,, ,,	,,	,,	8080	Grassi.
,, ,,	,,	,,	7900	Favre and Silbermann.
,, from sugar	,,	,,	8039·8	Andrews.
,, from wood	,,	Carbonic oxide	2473	Favre and Silbermann.
,, ,,	,,	,,	2227	,,
,, ,,	Protoxide of nitrogen	Carbonic acid and nitrogen	11158·2	Andrews.
Carbonic oxide	Oxygen..	Carbonic acid...	2402·7	Favre and Silbermann.
Hydrogen gas	,,	Water	34462	,,
,, ,,	,,	,,	33808	,,
,, ,,	,,	,,	34743	Andrews.
,, ,,	,,	,,	34666	Dulong.
,, ,,	Chlorine	Hydrochloric acid	23783·3	Grassi.
Marsh-gas (CH^2)	Oxygen.	Carbonic acid and water ...	13063	Favre and Silbermann.
,, ,,	,,	,,	13108	,,
Olefiant gas (C^2H^2)	,,	,,	11857·8	Andrews.
,, ,,	,,	,,	11942	Favre and Silbermann.
Alcohol, anhydrous	,,	,,	7183·6	Andrews.
,, ,,	,,	,,	6850	Favre and Silbermann.
Sulphur, native, in fine crystals, very pure	,,	Sulphurous acid	2220·9	Andrews.
,, native opaque	,,	,,	2249	Favre and Silbermann.
,, melted seven years previously	,,	,,	2216·8	,,
,, melted an hour after crystallization	,,	,,	2258·6	,,
,, in the soft state ½ an hour after melting	,,	,,	2253·2	,,
,, in the state of flowers	,,	,,	2307	,,
Bisulphide of carbon	,,	Carbonic and sulphurous acids	3400·5	Andrews.
Phosphorus	,,	Phosphoric acid	5747	Favre and Silbermann.
Zinc	,,	Oxide of zinc ...	1301	Andrews.
Iron	,,	Magnetic oxide?	4134	,,

fuel in the finest state of division with more litharge than it can reduce—20 parts at least, but not more than 40. Charcoal, coke, or

coal may be readily pulverized; but in the case of wood the fine sawdust produced by a fine saw or rasp must be employed. The mixture is put into the bottom of a close-grained conical crucible, and covered with 20 or 30 times its weight of pure litharge. The crucible, which should not be more than half full, is covered and heated gradually until the litharge is melted and evolution of gas has ceased. At first the mixture softens and froths up. When the fusion is complete the crucible should be heated more strongly for about ten minutes, so that the reduced lead may thoroughly subside and be collected into one button at the bottom. Care must be taken to prevent the reduction of any of the litharge by the carbonic oxide in the gases of the furnace. The crucible may now be taken out of the fire and left to cool. When cold it is broken, and the button of lead detached and weighed. If preferred, the melted contents of the crucible may be directly poured into a conical ingot-mould of metal. The accuracy of the result should be tested by repetition.

Forchhammer recommends the use of a mixture of 3 parts by weight of litharge and 1 of chloride of lead, instead of litharge only, as this mixture fuses at a much lower temperature than pure litharge, and does not corrode the crucible so much as litharge.[4]

ON THE CALORIFIC INTENSITY OF FUEL.

Suppose 1 gramme of carbon in the state of charcoal and 2·67 grammes of oxygen—that is, the exact proportion in which these elements combine to form carbonic acid—be brought together and combine; and suppose, further, that there is no loss of heat either by radiation or conduction. Now, if the specific heat of carbonic acid were the same as that of charcoal, its temperature after combustion would be found by dividing the number given as the calorific power of charcoal by the weight of the carbonic acid produced (1 + 2·67), and adding to the quotient the original temperature of the charcoal and oxygen—that of both being assumed to be the same. But the specific heat of carbonic acid is not the same as that of charcoal. It will therefore be necessary to multiply 3·67, the weight of carbonic acid produced, by its specific heat, in order to ascertain its temperature after combustion. For the sake of simplicity, in the following consideration, the temperature of all the elements concerned will be taken as at 0° C., at a constant pressure 0^m760 of mercury.

Let c = weight of charcoal in grammes,
p = calorific power of charcoal,
s = specific heat of carbonic acid,
T = temperature after combustion.

When the product of combustion is carbonic acid, the oxygen will always be $c \times 2{\cdot}67$.

pc = number of units of heat developed by combustion.

$$T = \frac{pc}{(c + 2{\cdot}67c)\,s}$$

[4] Berg. u. Hüttenm. Zeitung, 1846, p. 465.

This formula, it must be borne in mind, indicates the *theoretical* maximum temperature which charcoal is capable of producing by combustion in oxygen under conditions which can never occur in practice.

Let us now suppose that the combustion of charcoal is effected under the same conditions, by oxygen mixed with nitrogen, as in atmospheric air. The nitrogen is inert, and the effect of its presence would be simply to lower the temperature of the carbonic acid produced. Let n represent the weight of nitrogen in grammes, and s' its specific heat. Then

$$T = \frac{pc}{(c + 2 \cdot 67c)\, s + ns'}$$

Let us next suppose that water is present. The temperature would be much further reduced, especially by the abstraction of the heat which becomes latent in the conversion of water into steam, the state in which it must necessarily exist in the circumstances supposed. Let w represent the weight of water in grammes, s'' the specific heat of steam, and l its latent heat (see note [5], p. 61). Then

$$T = \frac{pc - wl}{(c + 2 \cdot 67c)\, s + ns' + ws''}$$

In the combustion of hydrogen by oxygen, let p' represent its calorific power and h its weight in grammes. Then

$$T = \frac{p'h - (h + 8h)\, l}{(h + 8h)\, s''}$$

In the determination of the calorific power of hydrogen, the water produced is in the state of vapour, which is subsequently condensed, so that its latent heat becomes sensible, and is estimated in the calorimeter. But in calculating the theoretic temperature resulting from its combustion, the latent heat must be deducted, for the reason already given.

In the combustion of charcoal and hydrogen conjointly, by oxygen mixed with nitrogen,

$$T = \frac{pc + p'h - 9hl}{(c + 2 \cdot 67c)\, s + 9hs'' + ns'}$$

When the combustion of the charcoal is imperfect and some carbonic oxide is formed, the temperature will suffer a corresponding reduction. Let c' represent the weight of charcoal converted into carbonic oxide, p'' its calorific power (= 2473), and s''' the specific heat of carbonic oxide. Then

$$T = \frac{pc + p''c' + p'h - 9hl}{(c + 2 \cdot 67c)\, s + (c' + 1 \cdot 33c')\, s''' + 9hs'' + ns'}$$

When a solid inert body is present, such as ashes in coal, its weight multiplied by its specific heat must be added to the divisor.

In the combustion of fuel in actual practice by atmospheric air, the

maximum theoretical temperature can never be attained, for the following reasons. Heat must be lost by *radiation*. In air-furnaces, which are chambers having a grate at the bottom and a flue at the top, much heat is lost by radiation from the grate. In blast-furnaces, which are chambers open at the top and closed at the bottom, with the exception of one or more small apertures through which air is blown in, the loss by radiation may be diminished by the absence of an open grate. But as the material of which furnaces are constructed must in the course of time become sensibly heated, so must there necessarily be loss of heat by radiation in all. There is loss of heat by *conduction*. This occurs not only through the matter forming the furnace, but also by means of the gaseous current which must be kept constantly flowing through the incandescent fuel. The loss will be unnecessarily increased if *too much air* is allowed to pass through the fuel; and there is reason to believe that in many cases loss from this cause may be greater than is generally supposed.

If we compare charcoal and hydrogen in respect to calorific *intensity*, we shall find that charcoal exceeds hydrogen, notwithstanding the converse is true in respect to calorific *power*. Let the calorific powers of charcoal and hydrogen be taken as 8080 and 34000 respectively, and the latent heat of steam at 537°,[5] and let it be required to find the calorific intensity of 1 gramme of each of these elements.

$$\text{In the case of charcoal } T = \frac{8080}{3{\cdot}67 \times 0{\cdot}2164} = 10173{\cdot}9^{\circ}$$

$$\text{In the case of hydrogen } T = \frac{34000 - (537 \times 9)}{9 \times 0{\cdot}475^{6}} = 6822{\cdot}7^{\circ}$$

$$\text{In the case of carbonic oxide } T = \frac{2403}{1{\cdot}57 \times 0{\cdot}2164} = 7072{\cdot}8^{\circ}$$

From these calculations, in which it is assumed that the specific heat of carbonic acid and the vapour of water is constant at all temperatures, it follows that in respect to calorific intensity the value of fuel is, *cæteris paribus*, great in proportion to the carbon which it contains. It is on this account that charcoal, coke, and the highly carbonaceous coals of South Wales may be so advantageously employed in the smelting of iron, which requires a very high temperature. The *combustibility*, however, of the charcoal or carbonaceous matter is an important element in this consideration. Graphite is pure carbon, yet, owing to its extreme incombustibility as compared with charcoal, its pyrometric effect would *practically* be very inferior to that of charcoal. The longer the time required for the combustion of any given fuel, the greater the loss of heat by radiation and conduction, and, consequently, the less the calorific intensity.

[5] The total heat of steam at 100° is, according to Regnault, 637, that is, *inclusive* of 100° from 0° to the boiling-point. But, as has been already mentioned, the temperature under the conditions supposed can never be below 100°, so that the actual amount of heat to be deducted is 637 − 100 = 537. Regnault, Chemical Reports and Memoirs, Cavendish Society, 1848, p. 273.

[6] Regnault.

CLASSIFICATION OF FUELS.

Wood	Soft.	
	Hard.	
Peat.		
Coal.....	Lignite	Bituminous wood.
		Brown coal.
	Bituminous coal	Non-caking, rich in oxygen.
		Caking.
		Non-caking, rich in carbon.
	Anthracite.	
Products of carbonization ...	Wood—charcoal.	
	Peat—charcoal.	
	Coal—coke.	
Combustible gases	Carbonic oxide.	
	Hydrogen.	
	Hydro-carbons.	

WOOD.

Wood is essentially composed of *organic tissue* and a small proportion of *inorganic matter;* and, in its ordinary state, it contains a large quantity of water, which may be completely expelled at a temperature much below that at which the decomposition of the organic part would occur. This tissue has the same elementary composition in all kinds of wood, though it may be associated with widely different kinds of organic matter in different species of trees. Thus, fir-trees contain turpentine, and oaks tannin. The organic tissue is essentially the combustible part of wood, as the associated organic matters are too small in quantity to produce any calorific effect of practical importance.

In external characters there is great variation in different kinds of wood: some are light, soft, and loose in grain, while others are heavy, hard, and close in grain. They have, accordingly, been divided into two classes—light and soft woods, like deal, and heavy and hard woods, like oak. The manner of burning of wood must, obviously, be connected with its external characters. Every one is familiar with the difference in this respect between deal and oak.

Kinds of wood employed as fuel.—It is but rarely that wood is directly employed as fuel in metallurgical operations requiring high temperatures, as the heat which it produces on combustion in its ordinary state is insufficient. It is, therefore, generally converted into charcoal. The choice of wood intended for burning must depend upon the nature of the trees which grow in the vicinity of the smelting works. In the following table is a list of the trees which most frequently occur in Europe:—

Botanical Name.	English Name.	French Name.	German Name.
Acer Pseudo-platanus, L. ..	Sycamore	Sycomore	Ahorn.
Betula alba, L.	White birch ...	Bouleau	Birke.
Alnus glutinosa, Gaertn. ...	Alder	Aune	Erle.
Carpinus Betulus, L.	Hornbeam	Charme	Hainbuche.
Fagus sylvatica, L.	Beech	Hêtre	Buche.
Fraxinus excelsior, L.	Ash	Frêne	Esche.
Populus tremula, L.	Poplar or aspen	Tremble	Espe.
——— nigra, L.	Black poplar ...	Peuplier noir...	Schwarzpappel.
——— fastigiata, Pers., regarded as a variety of P. nigra	Lombardy poplar	——— d'Italie	Italienische Pappel.
Quercus Robur, L.	Oak	Chêne	Eiche.
——— Ilex, L.	Evergreen oak	Yeuse	
Tilia Europæa, L.	Lime or linden-tree	Tilleul.....	Linde.
Æsculus Hippocastanum, L.	Horse-chestnut	Marronier d'Inde	Rosskastanie.
Salix alba, L.....	White willow...	Saule	Weisse Weide.
——— caprea, L.	Great round-leaved willow	Saule Marceau	Saalweide.
Ulmus campestris, L.	Elm	Orme	Ulme.
Abies excelsa, D.C.; syn. *Pinus Abies*, L.	Spruce fir	Faux sapin.....	Edeltanne.
——— pectinata, D.C.; syn. *Pinus Picea*, L.	Silver fir.....	Sapin commun	Fichte.
Larix Europæa, D.C.	Larch	Melèze.....	Lärche.
Pinus sylvestris, L.	Scotch fir	Pin sauvage, pin de Genève.....	Kiefer.

Elementary composition of wood.—The following table has been compiled from the results of Chevandier.[7] In every case a sample was prepared for analysis by collecting and mixing the sawdust produced by sawing billets in two from the top, middle, and bottom of the trunk; so that the mixture represented the average composition of every part of the trunk, inclusive of bark and alburnum. The sawdust was dried at 140° C., and placed in a dry vacuum until it ceased to lose weight.

ELEMENTARY COMPOSITION OF DRY WOOD.

Name of Tree.	Age and Part of Tree.	Exclusive of Ash.				Ash per cent.	Mean Composition exclusive of Ash.			
		Carbon.	Hydrogen.	Oxygen.	Nitrogen.		Carbon.	Hydrogen.	Oxygen.	Nitrogen.
Beech	70 years	49·89	6·13	43·09	0·88	0·86				
,,	58 ,, ...	49·96	6·02	42·79	1·23	1·00				
,,	69 ,, ...	49·75	6·04	43·09	1·12	0·88	49·89	6·07	43·11	0·93
,,	Branch wood	50·49	6·11	42·64	0·76	2·15				
,,	Shoots	49·62	6·12	43·58	0·67	1·29				

[7] Recherches sur la composition élémentaire des différents bois, et sur le rendement annuel d'un hectare de forêts. Par M. Eugène Chevandier. Ann. de Ch. et de Phys., 3, s. 10, p. 129. 1844.

ELEMENTARY COMPOSITION OF DRY WOOD—*continued.*

	Name of Tree.	Age and Part of Tree.	Exclusive of Ash.				Ash per cent.	Mean Composition exclusive of Ash			
			Carbon.	Hydrogen.	Oxygen.	Nitrogen.		Carbon.	Hydrogen.	Oxygen.	Nitrogen.
6	Beech	Faggots from young stems of 25 to 30 years old ...	51·15	6·31	41·74	0·80	1·50				
7	,,	Faggots from the branches of trees 70 to 80 years old	51·24	6·15	41·35	1·26	1·94	51·08	6·23	41·61	1·08
8	,,		51·06	6·22	41·75	0·97	1·71				
9	,,	Faggots from the branches of a tree 120 years old.	50·88	6·25	41·60	1·27	1·93				
10	Oak ...	120 years	50·97	6·02	41·96	1·05	2·43				
11	,,	From the branches of No. 10	51·01	6·00	41·72	1·26	2·03	50·64	6·03	42·05	1·28
12	,,	From young shoots of No. 10.....	50·09	6·07	42·31	1·52	1·68				
13	,,	Faggots from shoots 30 years old ...	50·82	6·23	41·98	0·97	1·45				
14	,,	Faggots from the branches of a tree 50 years old ...	50·73	lost.	lost.	0·99	1·56	50·89	6·16	41·94	1·01
15	,,	Faggots from a tree 70 years old ...	50·93	6·15	41·91	1·01	2·10				
16	,,	Faggots from a tree 130 years old ...	51·08	6·10	41·74	1·08	2·16				
17	Birch	60 years old...	50·59	6·21	42·16	1·03	0·71				
18	,,	From the branches of No. 17	50·79	6·29	41·48	1·44	1·03	50·61	6·23	42·04	1·1
19	,,	From the young shoots of No. 17 ...	50·48	6·20	42·43	0·89	0·60				
20	,,	Faggots from shoots 30 years old ...	52·21	6·36	40·24	1·19	1·16				
21	,,	Faggots from shoots 35 years old ...	51·61	6·32	40·95	1·12	1·54	51 93	6·31	40·69	1·0
22	,,	Faggots from the branches of trees 50 to 60 years old	51·97	6·25	40·89	0·89	1·26				
23	Poplar, Aspen	Branches and stem of a tree 25 years old. Average	50·31	6·31	42·39	0·98	1·86				
24	,,	Faggots from the branches of stems 25 years old ...	51·02	6·28	41·65	1·05	2·98				
25	Willow	From a shoot 20 years old	51·75	6·19	41·08	0·98	3·67				

ELEMENTARY COMPOSITION OF DRY WOOD—*continued.*

	Name of Tree.	Age and Part of Tree.	Exclusive of Ash.				Ash per cent.
			Carbon.	Hydrogen.	Oxygen.	Nitrogen.	
26	Willow.....	Faggots from branches of shoots 20 years old ...	54·03	6·56	37·93	1·48	4·57
	Mean	..	51·215	6·237	41·449	1·098	1·772

The next table is compiled from the results of Petersen and Schödler,[8] and those of Heintz: Nos. 27, 29, 31, 33, 34, 40, 41 are by Heintz.[9] The former were made in Liebig's laboratory, under his own inspection. A minute but unimportant error exists in these analyses, arising from the presence of a little carbonic acid in the ashes; but at the most it cannot exceed 0·2 per cent. Every specimen of wood analyzed was taken from the trunk.

ELEMENTARY COMPOSITION OF DRY WOOD.

	Name of Tree.	Exclusive of Ash.			
		Carbon.	Hydrogen.	Oxygen.	Nitrogen.
27	Oak, var. pedunculata	48·94	5·94	43·09	2·03
28	Oak.....	49·43	6·07	44·50	..
29	Beech.....	48·29	6·00	45·14	0·57
30*a*	,, red.....	48·18	6·28	45·54	..
30*b*	,, white	48·53	6·30	45·17	..
31	Birch	48·89	6·19	43·93	0·99
32	,, ...	48·60	6·37	45·02	..
33	Hornbeam	48·08	6·12	44·93	0·87
34	Alder	48·63	5·94	44·75	0·68
35	,, ...	49·20	6·22	44·59	..
36	Ash.....	49·35	6·07	44·56	..
37	Horse-chestnut	49·08	6·71	44·21	..
38	Black poplar	49·70	6·31	43·99	..
39	Lime	49·41	6·86	43·73	..
40	Scotch fir, old wood ...	49·87	6·09	43·41	0·63
41	,, young wood	50·62	6·27	42·58	0·53
42	,, ...	49·94	6·25	43·81	..
43	Spruce fir	49·95	6·41	43·65	..
44	Silver fir.....	49·59	6·38	44·02	..
45	Larch	50·11	6·31	43·58	..
46	Apple	48·90	6·23	44·83	..
47	Box	49·37	6·52	44·11	..
48	Walnut	49·11	6·44	44·44	..
	Mean	49·21	6·27	44·52*	..

* Oxygen, inclusive of nitrogen.

Proportion of water in wood.—All wood when recently felled contains a large quantity of water, which varies in amount with the nature of

[8] Ueber den absoluten Werth der gebräuchlichsten Holzarten als Brennmaterial; von Petersen und Schödler. Annalen der Pharmacie von J. Liebig u. and. 17, p. 139. Heidelberg, 1836. All the analyses are given in the Ann. d. Mines, 3, s. 11, p. 435.

[9] Brix. Untersuch. d. Heizkraft d. wichtigen Brennstoffe d. Preussischen Staates. Berlin, 1853.

the tree, the part of the tree, the season of the year at which it is felled, and, in trees of the same kind, with the place of their growth. When wood is exposed to the atmosphere during a sufficient length of time, under conditions favourable to desiccation, it loses the greater part of its water; but all kinds of wood, however well air-dried, retain on an average from 18 to 20 per cent. of water. This is a point of great practical importance in reference to the direct application of wood as fuel. The amount of hygroscopic water in wood may be ascertained by exposing it to a temperature between 100° and 150° C. until it ceases to lose weight. Violette has determined the proportion of water expelled from wood by desiccation at gradually increasing temperatures, and has given the results in the following table:[1]—

Temperature of Desiccation.	Water expelled from 100 parts of Wood.				Remarks.
	Oak.	Ash.	Elm.	Walnut.	
125° C.....	15·26	14·78	15·32	15·55	Between 200° and 225° there is slight decomposition, and water alone is not evolved. The statements in works on chemistry that wood contains a given quantity of water can only be exact in so far as they indicate the degree of desiccation.
150°.....	17·93	16·19	17·02	17·43	
175°.....	32·13	21·22	36·94	21·00	
200°.....	35·80	27·51	33·38	41·77	
225°.....	44·31	33·38	40·56	36·56	

The wood which Violette operated upon had been kept in store during two years. In each experiment the specimens were exposed during two hours to desiccation in a current of super-heated steam, of which the temperature was gradually raised from 125° to 225° C. When wood which has been strongly dried by means of artificial heat is left exposed to the atmosphere, it re-absorbs about as much water as it contains in its air-dried state.[2]

Af Uhr proved that the desiccation of wood by exposure to the atmosphere is much promoted by the removal of the bark. Trees were felled at the same time in June after the sap had risen, and the wood was left to dry under cover during the four following months; it was in pieces of unequal length and diameter, of which some were *barked* and others left with the *bark entire*. His results are recorded in the following table:—

	Loss per cent. of the original Weight of the Wood.			
	July.	August.	September.	October.
Barked stems.....	34·53	38·77	39·34	39·62
Unbarked stems.....	0·41	0·84	0·92	0·98

Thus, after the lapse of three months the barked wood was completely air-dried, whereas the unbarked wood had not even lost one per cent.[3]

[1] Ann. de Chim. et de Phys. 3, s. 39, p. 307.

[2] Schubarth, Handb. 3, p. 217.

[3] Anleitung zur vortheilhaften Ver-

The wood of the youngest branches of any individual tree contains about twice as much water as that of the trunk and older branches.

The following table presents the specific gravity of the wood of various trees, and the proportion of water which it contains before and after atmospheric desiccation :[4]—

Name of the Tree.	Specific Gravity.		Per centage of Water.	
	Freshly felled.	Air-dried.	Freshly felled.	Air dried.
Quercus Robur	1·0754	0·7075	34·7	16·64
—— var. pedunculata...	1·0494	0·6777	35·4	..
Salix alba	0·9859	0·4873	50·6	..
Fagus sylvatica.....	0·9822	0·5907	39·7	18·56
Ulmus campestris.....	0·9476	0·5474	44·5	18·20
Carpinus Betulus	0·9452	0·7695	18·6	..
Larix Europæa	0·9205	0·4735	48·6	..
Pinus sylvestris.....	0·9121	0·5502	39·7	..
Acer Pseudo-platanus ...	0·9036	0·6592	27·0	18·63
Fraxinus excelsior	0·9036	0·6440	28·7	..
Betula alba	0·9012	0·6274	30·8	19·38
Pyrus Aucuparia ..... (Mountain-ash.)	0·8993	0·6440	28·3	..
Abies excelsa.....	0·8941	0·5550	37·1	17·53
—— pectinata	0·8699	0·4716	45·2	..
Pyrus torminalis ..... (Wild service tree.)	0·8633	0·5910	32·3	..
Æsculus Hippocastanum	0·8614	0·5794	38·2	..
Alnus glutinosa.....	0·8571	0·5001	41·6	..
Tilia Europæa	0·8170	0·4390	47·1	18·97
Populus nigra	0·7795	0·3656	51·8	..
—— tremula.....	0·7654	0·4302	43·7	..
—— fastigiata	0·7634	0·3931	48·2	19·55
Salix caprœa	0·7155	0·5289	60·0	..

The degree of dryness will necessarily vary with the state of the atmosphere as to moisture. By air-drying wood may shrink $\frac{1}{16}$ in volume, or perhaps more.[5]

The proportion of water in wood is least at the fall and beginning of the year, as will appear from the following results :[6]—

Kinds of Wood.	Proportion of Water.	
	Jan. 27.	April 2.
Abies excelsa.....	52·7	61·0
Corylus Avellana	40·9	49·2
Æsculus Hippocastanum.....	40·2	47·1
Acer Pseudo-platanus	33·6	40·3
Fraxinus excelsior	28·8	38·6

kohlung des Holzes in stehenden und liegenden Meilern von Carl David af Uhr. Aus dem Schwedischen übersetst v. Dr. J. C. L. Blumhof. Giessen, 1820, p. 13.

[4] Extracted from Schubarth's Handb. 3, p. 217. It is prepared from the data obtained by Schübler and Neuffer, and Rumford.

[5] Syst. d. Metal. Karsten, 3, p. 23.

[6] Schübler and Neuffer, System d. Metallur. Karsten, 3, p. 21.

According to Werneck the wood of trees which have grown on mountains, under the same conditions, is more compact than that grown in plains; the wood of closely-grown trees is more compact than that of isolated trees; and the compactness appears to increase in proportion to the dryness of the soil.[7]

Specific gravity of wood.—Wood being extremely porous, its specific gravity must necessarily vary according to the amount of water which it contains: as the water evaporates, the spaces which it occupied become filled with air, except in so far as they are contracted by shrinking. From the fact of all woods having nearly the same elementary composition, it might be anticipated that the specific gravity of all would be nearly the same; and this is found to be the case when the determination is made with wood of which the pores have been completely deprived of air and afterwards filled with water. The variations in specific gravity, which appear in the preceding table, are in great measure due to the variable proportions of air and water contained in the pores of the wood. After complete expulsion of air, Rumford obtained the following results:—

	Specific Gravity.		Specific Gravity.
Oak	1·5344	Pine	1·4621
Elm	1·5186	Birch	1·4848
Beech	1·5284	Lime	1·4846
Sycamore	1·4599	Poplar	1·4854

By immersion in water, and subsequent drying, the specific gravity of wood is somewhat diminished. Thus, Werneck found that the specific gravity of beech-wood was 0·56, which, after the wood had been transported by floating in water, was reduced to 0·537; and that similarly the specific gravity of spruce fir was reduced from 0·493 to 0·464.[8]

Proportion of ashes yielded by wood.—This subject has been investigated by many observers, and by no one in a more complete and satisfactory manner than by Chevandier, to whom we owe the following average results of not less than 524 incinerations.[9]

Name of the Wood.	Number of Incinerations.	Mean percentage of Ashes.
Willow	17	2·00
Aspen	59	1·73
Oak	93	1·65
Hornbeam	73	1·62
Alder	26	1·38
Beech	93	1·06
Scotch fir (pin)	28	1·04
Silver fir (sapin)	46	1·02
Birch	89	0·85

[7] Karsten, op. cit. p. 19. Ueber Verkohlung des Holzes, etc. F. Klein, p. 92. Gotha, 1836.

[8] System d. Metall. Karsten, 3, p. 22.

[9] Comptes Rendus, 24, p. 269. 1847.

The *general* average percentage of ashes of all these woods taken together is as follows:—

Quality of the Wood.	Percentage of Ashes.
Entire wood[1] of young shoots	1·23
Wood split into billets[2]	1·34
Entire wood of branches	1·54
Faggots of twigs	2·27

The geological character of the ground does not appear to exert a decided influence on the proportion of ashes, at least in the case of hard woods. The variation in the proportion of ashes found by Chevandier to occur in the different specimens of wood which he analysed indicates that this inorganic constituent of wood is affected by the nature of the ground and by that of the waters which moisten the roots.[3] Wood from different parts of an old tree contains a variable proportion of ashes: the trunk contains the least, and the small branches the most; young shoots generally contain less than old trees. The inorganic matter may not be equally distributed in the same piece of wood: thus, one portion yielded 2·64 per cent., and another only 0·69. The same result occurred in the incineration of 10 other specimens.[4]

Composition of the ashes of wood.—Although numerous analyses of the ashes of various kinds of herbaceous plants are recorded, yet I have found but few of the ashes of wood; and of these scarcely one can be regarded as complete. The following will suffice for illustration:—

	Composition of the Ashes of Wood.					Composition of the Ground.		
	1.	2.	3.	4.	5.	6.	7.	8.
Potash	12·81	5·67	14·78	6·94	10·91	0·03	0·06	0·81
Soda	1·60	1·25	2·77	0·34	1·23	0·03	0·05	0·77
Lime	26·72	46·89	..	43·59	13·55	50·95	0·49	4·21
Magnesia	2·22	1·69	11·78	5·39	12·03	2·11	0·49	2·77
Alumina	1·38	0·42	..	..	0·05	0·78	..	11·46
Sesquioxide of iron	0·78	0·47	..	0·62	..	6·02	0·49	15·15
Protoxide of manganese	trace	1·67	3·81	trace	3·47	..	0·02	..
Silica	2·88	1·51	4 00	2·13	6·36	7·07	3·24	12·49
Carbonic acid	18·83	24·67	12·92	28·29	26·24	10·20	..	1·32
Phosphoric acid	8·13	4·22	16·65	7·54	5·64	trace	0·03	..
Sulphuric acid	0·02	..	2·77	0·62	1·04	..	..	0·01
Chlorine	..	..	..	..	..	..	trace	0·03
Residue insoluble in acid	7·17	7·17	9·84	0·62	6·68	18·81	94·49	39·88
Water	19·84	2·40	4·67	3·66	10·71	3·99	1·52	11·10
Charcoal	0·62	0·46	0·49	..	2·08	..	..	..

In Liebig and Kopp's Jahresbericht, from which I have extracted these analyses, the sum of the constituents under each of the first five columns is given as exactly 100·00, but the addition is incorrect. The proportion of water in the first and fifth analyses must surely be erroneous. The analyses were originally published in the Chemisch-Pharmaceutisches Centralblatt for 1851. Unfortunately I have not been able to refer to this work and correct the errors. It is not in any of the following Libraries: Royal Society, Royal Institution, College of Surgeons, British Museum, and not even in that of the *Pharmaceutical Society!*

[1] Rondinage de jeunes brins. Bois de rondinage means wood sawn across in lengths, but not split into billets.

[2] Bois de quartier. This term is applied to wood cut in lengths, each of which is split into two or more billets.

[3] Ann. de Chim., 3, s. 10, p. 150.

[4] Comptes Rendus, 24, p. 420.

These analyses were made by Witting, under the direction of Genth. Nos. 6–8 are analyses by the same chemist of the ground on which the trees grew. Nos. 1–3 are of the ashes of *birch*, and Nos. 4, 5 of the ashes of *beech*. No. 1 grew on ground No. 8; No. 2 on ground No. 6; No. 3 on ground No. 7. No. 4 grew on ground No. 6; and No. 5 on ground No. 7. No. 6 at Morschen, Hesse-Cassel, on the Muschelkalk formation; No. 7 at Marburg, in the same State, on Buntersandstone; and No. 8 at Akureyri in America, on a formation of volcanic palagonite origin.[5]

The presence of alumina is remarkable. Phosphoric acid is not mentioned in the ground No. 8, and yet it must have been present, because it existed in the ashes of the tree which grew upon that ground. In No. 6 only part of the lime could have been combined with carbonic acid; and as to the state of combination of the other part, no evidence is advanced. These analyses are instructive as showing the influence of the nature of the ground upon the so-called inorganic constituents of trees.

Composition of the Ashes of Wood.

	1.	2.	3.	4.
Potash	15·80	2·79	0·93	15·24
Soda	2·76	15·99	14·59	7·27
Lime	60·35	30·36	33·99	25·85
Magnesia	11·28	19·76	20·00	24·50
Oxide of manganese (Mn^3O^4)	..	18·17	7·61	13·51
Phosphate of sesquioxide of iron ($2Fe^2O^3$, $3PO^5$)	1·84	5·10	2·28	6·18
Sesquioxide of iron	..	..	7·73	..
Phosphate of lime ($3CaO$, PO^5)	3·99	..	..	..
Sulphate of lime	2·30	3·31	5·05	2·91
Chloride of sodium	0·21	1·48	2·52	0·92
Silica	1·46	3·04	5·27	3·60
	99·99	100·00	99·97	99·98
Ash per cent. in the wood dried at 100° C.	..	0·143	0·190	0·322

These analyses were made by Böttinger at Giessen, under the direction of Will. No. 1. Fagus sylvatica, from Neufchâtel, Switzerland. Nos. 2, 3. Pinus sylvestris, from the vicinity of Giessen, not far from which are dolomite and mines of manganese. The ashes of Nos. 2, 3, 4 were brown-black, and evolved chlorine copiously when heated with hydrochloric acid. No. 2 was diseased. The ashes of No. 3 were obtained from a tree which had died. No. 4. Larix Europæa, from the same locality as Nos. 2, 3. In these analyses the calculation has been made after deduction of carbonic acid, charcoal (from imperfect incineration), and sand; but, if proper precautions had been observed in the preparation of the ashes, it is difficult to understand how *sand* should be present in them.[6]

[5] Jahresbericht, Liebig u. Kopp, for 1851, p. 708.

[6] Annalen der Chemie und Pharmacie, Wöhler and Liebig, 50, p. 406. 1844.

On the rapidity of growth of wood.—On this subject there are many recorded observations, from which, on account of their importance to the metallurgist in some countries, I introduce a selection.

Chevandier ascertained that on the western slope of the Vosges mountains and in the plain extending from their base, where the grès bigarré (lower trias) occurs, the average annual production of wood in forests of large beech-trees is about 9 stères (1 st. = 1 cubic metre = 317·849 cub. feet) per hectare (10,000 square metres, nearly 2½ acres). The average weight of dry wood annually produced in these forests amounts to 3650 kilogrammes (8047 lbs. avoird.), which contain 1800 kil. (3968 lbs.) of carbon and 26 (57 lbs.) of hydrogen in excess of that required to form water with the oxygen of the wood. He has calculated that a bed of coal (containing 85 per cent. of carbon) corresponding to the annual growth of these forests per hectare, would have an average thickness of $0^{m}000165$ (0·006496 inch).[7]

The produce of coppice wood (taillis) is much influenced by the nature of the ground; the more permeable and hygroscopic it is, the greater the produce. But in woods of large trees the geological influence of the ground disappears. The difference is explained by the fact that in coppices the ground is not so protected from the desiccating action of the sun as in woods, so that it does not so long retain the necessary moisture, and the vegetative season is, consequently, shortened. Chevandier has shown that the influence of moisture is so considerable that silver firs (sapins) raised in boggy ground only grow at the rate of $1^{kil}·80$ (3·968 lbs.) a year; in dry ground at the rate of $3^{kil}·40$ (7·496 lbs.) a year; when watered by rain at $8^{kil}·20$ (18·078 lbs.) a year; and when watered by running streams at $11^{kil}·60$ (25·573 lbs.) a year.

The maximum of growth in different trees is stated by Chevandier to be as follows: oak at 77 years; ash at 80 years; silver fir (sapin), in very good ground, at 115 years; in ground of medium quality at 76 years; Scotch fir, in good ground, at 51 years; and in ground of medium quality 50 years. The difference in the last case is remarkably small!

In the Black Forest in the Duchy of Baden trees of hornbeam produced annually 2560 kil. (5644 lbs.) of dry wood per hectare (2½ acres), and trees of silver fir (sapin) 3903 kil. (8604 lbs.).[8] These numbers include the wood obtained in thinning the forests, which is estimated at 15 per cent. in addition to the wood obtained in felling the trees. The actual data are recorded in the table on page 72.

In Sweden and Norway the forests chiefly consist of Scotch fir; spruce fir and birch occur in much less proportion, and even the silver fir is not common in several provinces. The annual yield varies considerably, ranging from 3 to 8 stères per hectare (105·950 to 282·533 c. f. per 2½ acres). In those parts of Sweden which do not notably exceed 60° of latitude, 6 stères (211·900 c. f.) may be taken as the average.

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[7] Ann. de Chim., 3, s. 10, p. 156.
[8] Chevandier, Comptes Rendus, 24, p. 275. 422. 1847.

FORESTS OF THE GRAND DUCHY OF BADEN.[9]

	Kind of Wood.	Mean Annual Growth per Hectare (2·4711, say 2½ acres) in Cubic Metres (cub. feet 35·3166) in *actual* volume.	Number of Cubic Metres (Stères) corresponding in *apparent* volume.	Dry Wood, corresponding in Kilogrammes and Pounds.
Gneiss, granite, porphyry, grès bigarré (lower trias), marnes irisées (upper trias), vieux calcaire jurassique, rolled flints	Oak	5 221 184·388 cubic feet.	7·57	2900·81 6395 lbs.
Gneiss, granite, grès rouge, grès bigarré, vieux calcaire jurassique (lower jurassic limestone), nouveau calcaire jurassique (upper jurassic limestone), molass	Ash (mountains of medium altitude)	5·224 184·594 c. f.	7·57	2994·28 6601 lbs.
Gneiss, granite, porphyry, terrain de transition, nouveau calcaire jurassique	Ash (high mountains)	4·559 161·008 c. f.	6·61	2574·62 5676 lbs.
Rolled flints	Hornbeam (charme)	4·008 141·549 c. f.	5·81	2226·04 4907 lbs.
Gneiss, granite, grès bigarré, muschelkalk	Silver fir (sapin)	8·304 293·269 c. f.	12·04	3394·21 7483 lbs.
Granite, grès bigarré, muschelkalk, rolled flints	Scotch fir (pin)	7·330 158·871 c. f.	10·63	2798·71 6170 lbs.

In latitudes bordering on 60° the diameter of a pine (pin) 25 years old is only 11 centimetres (4·33 inches): whereas on tolerable land in France and Germany the annual growth during this first stage of the life of the tree is half as much again. Wood intended for the smelting-works is cut at intervals, which vary with the locality, from 25 to 60 years; and when it is to be converted into charcoal, it appears most advantageous to cut the trees at the age of 30 years.[1]

Weight of wood.—The following determinations have been made in Prussia of the weight of a cubic foot, in pounds (Prussian),[2] of various kinds of wood in different states of dryness:[3]—

	Quite fresh.	Half dry.	Quite dry.
Oak	70	60	46
Beech	65	50	39
Birch	60	50	42
Hornbeam	62	56	50
Scotch fir	60	48	36–26

Practical directions for the cutting and storing of wood intended as fuel.—The trees should be of mature growth, and should be felled when most

[9] In this table no account is taken of the intermediate products resulting from thinnings (éclaircies), which would increase the numbers given above by about 15 per cent.

[1] Sur l'Exploitation des Mines et des Usines dans le Nord de l'Europe. Par M. J. Durocher. Ann. des Mines, 5, s. 9, p. 356. 1856.

[2] 1 foot English = 11·65368 inches Prussian.
1 cubic do. = 1582·667 cubic inches do.
1 pound Prussian = 1·03123623 pound avoirdupois.

[3] Bergwerksfreund, 3, 8.

free from sap. The wood should be cut to a suitable length, and should be so stacked as to allow the air freely to circulate through the pile, in order to promote desiccation as much as possible. If uncleaved in the direction of its length, it should be previously deprived of bark, either wholly or partially, by taking it off in strips all round. It should be protected from wet and rain; if transported to a distance in rafts, it should not be left in the water longer than absolutely necessary, because experience has proved that its value as fuel deteriorates by long soaking.

PEAT OR TURF.

Peat is the product of the natural decay of various kinds of plants under special conditions of heat and moisture which occur in humid and temperate climates. Immense accumulations of peat constituting *peat bogs* exist in this country, especially Ireland. Peat is abundant in the northern and central parts of France, and in various other parts of Europe. It is found on mountainous declivities where it seldom exceeds four feet in thickness, and in low grounds where it may exceed even forty feet in thickness. It does not appear to exist within the tropics, yet the "Great Dismal" Swamp, in 36° 8′ lat., between Virginia and North Carolina, consists of black peat-like matter without any admixture of earthy particles, to the depth of fifteen feet.[4] The peat of Europe is chiefly derived from mosses belonging to the genus Sphagnum; but that of South America contains no remains of mosses. In the sequel will be given the analysis of peat which my friend Dr. Falconer obtained from the bottom of a lake in Cashmere, and which is also free from the remains of mosses. It is certain that many peat bogs occupy the site of former forests; and hence they occasionally contain imbedded trunks of trees, sometimes of very large dimensions. As peat is composed of the tangled remains of plants in different stages of decay, it may be more or less *fibrous* or *earthy*. It varies much in texture, but is generally so spongy as to retain a large quantity of water. The deeper the peat is taken from the bog, the more condensed and changed is the vegetable structure, of which, however, sufficient always remains to be readily distinguishable.[5] It is composed of the same elements as woody tissue, with variable proportions of water and inorganic matter. This matter is in part derived from the inorganic constituents of the plants from which the peat has originated; but it may occasionally be much increased by the presence of extraneous substances carried by streams or floods into the bog.

Specific gravity of peat.—It must obviously be subject to much variation from several causes, such as difference in structure, degree of

[4] Principles of Geology. Sir C. Lyell. 1853. p. 724.

[5] Dr. Bennett. Trans. of the Royal Soc. of Edinburgh, 1854 v. 21. p. 183.

desiccation, proportion of earthy matter, state of decomposition, and mode of preparation. According to Vogel, the specific gravity in some kinds is as low as 0·25, while in others which have not been compressed it ranges from 0·6 to 0·9.[6]

COMPOSITION OF PEAT.

No.	Locality.	Specific Gravity.	Carbon.	Hydrogen.	Oxygen.	Nitrogen.	Sulphur.	Ash.	Water.	Charcoal or Coke.	Exclusive of Ash.		
											Carbon.	Hydrogen.	Oxygen, inclusive of Nitrogen.
1	Cappoge, Ireland .	..	51·05	6·85	39·55	..	..	2·55	..	26·37	52·38	7·03	40·59
2	Kilbeggan, do. .	..	61·04	6·67	30·46	..	..	1·83	..	21·50	62·18	6·99	31·03
3	Kilbaha, do. .	..	51·13	6·33	34·48	..	..	8·06	..	..	55·62	6·88	37·50
4	Phillipstown, do. .	0·405	58·69	6·97	32·88	1·45	..	1·99	..	..	..	..	..
5	Do. do. .	0·669	60·48	6·10	32·55	0·88	..	3·30	..	..	..	..	..
6	Wood of Allen, do.	0·335	59·92	6·61	32·21	1·26	..	2·74	..	..	..	..	..
7	Do. do.	0·639 to 0·672	61·02	5·77	32·40	0·81	..	7·90	..	..	..	..	..
8	Devonshire . . .	0·85	54·02	5·21	28·17	2·30	0·56	9·73	25·56	29·30	59·74	5·77	31·32*
9	Abbeville, France .	..	57·03	5·63	29·55	2·21	..	5·58	..	..	60·40	5·96	33·64
10	Do. do. .	..	58·09	5·93	31·37	..	..	4·61	..	..	60·89	6·21	32·90
11	Framont, do. . .	..	57·79	6·11	30·77	..	..	5·33	..	..	61·05	6·45	32·50
12	Thésy, do. . . .	..	59·67	5·76	34·95	1·92	..	6·70	..	36·95	54·31	6·17	39·52
13	Camon, do. . . .	..	46·11	5·99	35·87	2·63	..	9·40	..	38·11	50·89	6·61	42·50
14	Cashmere . . .	..	33·28	3·66	21·03	1·81	..	29·81	10·40	..	55·66	6·12	38·22

* Exclusive of nitrogen and sulphur.

1 to 3.[7] Sir R. Kane states that it is very usual to find the turf of commerce containing one-fourth of its weight of water; and that when it is dried in the air, under cover, it still retains one-tenth of its weight.

4.[8] Light surface peat, of a pale reddish-brown colour, containing small roots of Erica (heath) and leaves of grasses and Carex (sedges). Average thickness of the bog 18 feet; area 6582 acres.

5. Rather dense peat from the same bog as the last. Colour dark-reddish brown. Structure of moss still distinguishable, but species difficult to be determined.

6. Light surface peat, pale yellowish brown, moss very open-grained and fibrous. Principally composed of Sphagnum, Hypnum, etc., the species of which may readily be distinguished.

7. Lower layer of the same bog as the last. Compact and dense. Colour deep blackish-brown. Fracture earthy, appearing almost con-

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[6] Der Torf, seine Natur und Bedeutung. Eine Darstellung der Entstehung, Gewinnung, Verkohlung, Destillation und Verwendung desselben als Brennmaterial. Von Dr. August Vogel, Professor in München. Braunschweig, 1859, p. 24. This is a comprehensive treatise in 170 pages, well illustrated with wood-engravings: it might be advantageously translated into English.

[7] By Sir Robert Kane, 'The Industrial Resources of Ireland,' 1845, p. 37.

[8] 4–7. Report on the Nature and Products of the process of the Destructive Distillation of Peat, considered specially with reference to its employment as a branch of manufacturing industry. By the Director of the Museum of Irish Industry (Sir R. Kane). 1851.

choidal, and exhibiting a resinous lustre when rubbed. All appearance of vegetable matter totally obliterated.

8.[9] Cut for fuel from the neighbourhood of the Military Prison, Princetown, near Tavistock, Dartmoor, Devonshire. Colour earth-brown; porous and largely intermingled with vegetable fibres of a light-brown colour, hard enough to be cut with a knife. When heated the gas gives a brilliant flame with much smoke; the residual coke is much shrunk in bulk, but retains the shape of the pieces employed; it is without lustre and pulverulent, and is readily converted into a light bulky ash of a pure white colour, quite infusible before the blow-pipe.

9.[10] Was in a very advanced state of change; it presented here and there some fragments of vegetables which had kept their form. Colour very dark brown; powder, brown. 1·23 of ashes contained 0·90 of carbonate of lime and 0·33 of clay. The lime did not exist as carbonate in the peat, but was combined, Regnault believes, with some organic acid, such as the so-called humic. The carbon, therefore, of the carbonic acid of the carbonate of lime is added to that obtained on the combustion. Before this correction the ash was 8·20 per cent. The peat was from Vulcaire, near Abbeville.

10. Similar to No. 4, from Long, near Abbeville. A similar correction was made in this analysis for the carbonic acid in the ashes.

11. From Champ-du-Feu, near Framont (Vosges). This peat was in a little less advanced state of change than Nos. 4 and 5.

12.[1] Black peat of first quality. Previously to analysis, air dried during many months and in a dry vacuum during 24 hours.

13. First quality. Dried for analysis like No. 12.

14.[2] This peat was taken by my friend Dr. Hugh Falconer from the bottom of a lake in Cashmere. It contains the remains of the roots of aquatic plants free from those of mosses. Two analyses were made.

Composition of the Ashes of Peat.—A series of not less than 27 analyses of the ashes of peat from various localities in Ireland has been made in the laboratory of the Museum of Irish Industry, under the direction of Sir Robert Kane; and of these I insert the four following of the ashes of the varieties of peat, numbered 4, 5, 6, 7 in the preceding table of the composition of peat.[3] (See Table, p. 74.)

It is stated that the quantity of carbonic acid found by experiment was nearly in every case much less than that required to saturate the lime, admitting the whole of the sulphuric acid to exist in sulphate of lime; and it is inferred that the greater part of the carbonic acid, which is supposed to have been in combination with lime, was expelled during incineration.[4] According to Regnault the lime in peat is certainly not present in the state of carbonate, but is in

[9] By Vaux. Jo. Chem. Soc. vol. i. p. 318.

[10] 9-11. By Regnault. Ann. des Mines, 3. s. 12. p. 230. 1837.

[1] 12, 13. By M. de Marsilly. Ann. d. Mines. 5. s. 12. p. 406. 1857.

[2] By C. Tookey, in my laboratory.

[3] Report ante cit. 1851. p. 72.

[4] Op. cit. p. 72.

	4.	5.	6.	7.
Potash	1·323	0·461	0·491	0·247
Soda	1·902	1·399	1·670	0·496
Lime	36·496	40·920	33·037	24·944
Magnesia	7·634	1·611	7·523	1·285
Alumina	5·411	3·793	1·686	0·360
Sesquioxide of iron	15·608	15·969	13·281	19·405
Phosphoric acid	2·571	1·406	1·438	0·242
Sulphuric acid	14·092	14·507	20·076	10·742
Hydrochloric acid	1·482	0·983	1·747	0·335
Silica in compounds decomposable by acids	3·595	1·111	2·148	1·082
Sand and silicates undecomposable by acids	2·168	2·107	7·683	26·789
Carbonic acid	7·761	15·040	8·340	13·890
	100·043	99·307	99·120	98·817

combination with an organic acid, such as the so-called humic or ulmic acid; for he states that no effervescence occurs by the addition of an acid to peat.[5]

Iron pyrites may be expected to occur in peat, and Karsten states that some kinds of peat contain so large an amount of this sulphide that they have been profitably employed in the manufacture of sulphate of iron.[6]

In peat occurring near Moel-Hafod-Owen, North Wales, copper was found in sufficient quantity to be profitably extracted. The peat was pared off the surface of the bog and burned in kilns, and from the ashes the copper was separated. Many thousand pounds worth of the metal were thus procured.[7]

Complete Analysis of Peat.—The following analysis of a brown fibrous peat from St. Wolfgang in Upper Austria has been made by Ferstl.[8]

1. Soluble in water:—

a. *Organic matter* with trace of ammonia			1·500
b. *Inorganic matter:*			
Sulphate of lime	0·041		
Chloride of potassium	0·008		
Chloride of sodium	0·007		
Chloride of magnesium	0·049		
Sesquioxide of iron	0·015		
Alumina	0·013		
Silica	0·026	0·159	1·659

[5] Ann. d. Mines, 3. s. 12. p. 231.
[6] Sys. 3. p. 91.
[7] Professor A. C. Ramsay. Journal of the Geological Society. 10. p. 245. 1854.
[8] Kenngott. Uebersicht. Published 1856. p. 153. Extracted from the Jahrb. d. k. k. geol. Reichsanstalt. 4. p. 152.

2. Soluble in hydrochloric acid :—

a. *Organic matter*		0·126	
b. *Inorganic matter :*			
Phosphoric acid	1·070		
Lime	1·052		
Magnesia	0·295		
Sesquioxide of iron	0·122		
Protoxide of manganese	0·047		
Alumina	0·312		
Silica	0·046	2·944	3·070

3. Insoluble in water and acid :—

a. *Organic matter :*			
Humic acid	22·600		
Humic carbon	37·700		
Resin	4·100		
Wax	1·400		
Vegetable fibre	16·220		
		82·020	
b. Inorganic matter		0·290	
c. Water		14·500	
d. Carbonic acid not determined			96·810
		Total ...	101·539

The air-dried peat gave—

Water	14·50
Ash	3·48
Organic matter	82·02
	100·00

Desiccation of Peat.—M. de Marsilly found that thoroughly air-dried peat lost by desiccation in a dry vacuum from 2·17 to 7·20 per cent. of its weight, and in a waterbath at 100° C. from 12 to 20 per cent. He also ascertained that at 120° C. peat suffers decomposition, with the disengagement of products containing carbon and hydrogen in excess of that required to form water, with the oxygen in those products. At 250° C., according to the same observer, peat often ignites.

Extraction and Preparation of Peat.—Peat is cut out of the bog in rectangular pieces, with which every one is familiar. These are stacked in heaps so that they may be thoroughly air dried. Various methods have been proposed to improve the quality of peat as fuel, of which one of the most successful appears to be that of grinding the peat in a pugmill, and then moulding the pulp thus produced into bricks. The bricks are first dried in the air and afterwards in stoves. This method is in operation at Ekman's iron-works in Sweden, and has been fully described in the 'Jern-Kontorets Annaler' for 1858, and in 'Tunner's Jahrbuch' for 1860. Substantially the same process was patented by Linning in 1837.[9] I insert the following extracts from the specification of this patent :—"I in the first place reduce the mosses

[9] Specification. A.D. 1837. No. 7,296.

to a homogeneous pulpy mass, nearly in the same manner as brick makers reduce their plastic material to a uniform state, namely, by passing through what they call a puggy mill, but which I fit with longer and sharper knives, somewhat obliqued. * * * I then convey the moss so prepared to and place it on a table, platform, or floor, to be cut or moulded like bricks into any size or shape, either by the hand or by mechanical means. * * * These blocks or pieces are then exposed or subjected to more or less pressure by means of levers, screws, hydraulic presses, or other compressing power or apparatus, and transferred to and arranged in a close chamber heated by flues or a stove, or to a kiln, in order that they may dry or consolidate from the evaporation of the moisture they contain. Exposure in this manner to an artificial heat produced by or obtained from the substance itself, and raised from 70 to 120 Fah. degrees or higher for a period of 24 hours, will probably be sufficient to dry the manufactured article completely, as will be easily discernible, and which is obtained in a very hard and dense state, and may be used for the same purposes as pit-coal, with the advantage that it is free, at least generally so, from sulphur (?):"

In localities where good coal is abundant and can be obtained at a moderate price, it is hardly to be expected that the process of compressing peat should be profitably conducted. The expense of suitable machinery and the price of labour required for the operation are necessarily very considerable. In some countries, however, which do not, like Great Britain, possess valuable and extensive coal fields, compressed peat may be employed with advantage, especially as fuel for raising steam. It has been for some years applied under locomotive boilers in Bavaria; but before this application was brought to a successful issue many difficulties had to be encountered.[1] At Rosenheim, in South Bavaria, peat, after having been freed from roots, &c., is passed through rolls, dried and heated to about 100° C., and being thus obtained in a pulverulent state, is introduced into the pressing machine, and manufactured into bricks weighing from 8 to 10 ounces each. By this process peat is rendered five times more dense.[2] It is not advisable to apply very great pressure, as the cost would be thereby so much increased as to render the manufacture unprofitable. A Bavarian cubic foot (= 11½ inches) of the compressed peat weighs from 60 to 70 lbs. (nearly the same weight English).

COAL.

In the year 1853 a remarkable trial took place at Edinburgh before the Lord Justice-General and a special jury to try the question "What is coal?" The owner of an estate had granted a lease of the *whole coal* contained in it. In the course of working, the lessees extracted a combustible mineral of great value as a source of coal-gas, and they realized a large profit by the sale of it as gas-coal. The

[1] Vogel, op. cit. p. 33.

[2] Jahresbericht. Wagner, 1861, p. 618.

lessor then denied that the mineral in question was coal, and disputed the right of the lessees to work it. At the trial there was a great array of scientific men, including chemists, botanists, geologists, and microscopists; and of practical gas-engineers, coal-viewers, and others there were not a few. On the one side it was maintained that the mineral was *coal*, and on the other that it was a *bituminous schist*. The evidence, as might be supposed, was most conflicting. The judge, accordingly, ignored the scientific evidence altogether, and summed up as follows:—"The question for you to consider is not one of motives, but what is this mineral? Was it coal in the language of those persons who deal and treat with that matter, and in the ordinary language of Scotland? *because, to find a scientific definition of coal after what has been brought to light within the last five days, is out of the question.* But was it coal in the common use of that word, as it must be understood to be used in language that does not profess to be the purest science, but in the ordinary acceptation of business transactions reduced to writing? Was it coal in that sense? That is the question for you to solve." The jury found that it was coal.[3] Since this trial the same mineral has been pronounced *not to be coal* by the authorities of Prussia, who accordingly have directed it not to be entered by the custom-house officers as coal.[4]

From what precedes it is evident that it is not easy to frame a precise definition of the term coal, either in a commercial or in a scientific sense. The substances to which the term coal is usually applied differ widely both in physical and chemical characters. All coal results from the decomposition of vegetable matter under special conditions, and in degree of decomposition there is every stage. Thus, at one extreme is lignite, some varieties of which closely resemble wood both in composition and appearance; and at the other is anthracite, which consists almost wholly of carbon, and is, in all respects, unlike wood. Again, the proportion of earthy matter, or ash, in coal is subject to great variation. Suppose a mineral to consist of 5 per cent. of coal-like, black, combustible matter, in all respects similar to undoubted coal, and of 95 per cent. of earthy matter. No one would designate such a mineral as coal. Then the question arises, what is the *maximum* amount of such matter which can exist in coal? No definite answer can be given. In the present state of science I do not believe it possible to propose an exact definition of the term coal. Geological position does not afford satisfactory grounds for a precise definition, for the mineral which was the subject of investigation at the trial in Edinburgh occurs in association with coal of the true coal-measures; and true coal, so far as may be inferred from the assemblage of chemical and physical characters, is met with in other and more recent geological formations.

[3] A full report of the trial before the Lord Justice-General and a special jury of the issues in the action and at the instance of Mr. and Mrs. Gillespie of Torbanehill against Messrs. Russel and Son, coal-masters, Blackbraes, for infringement of lease of coal and ironstone, etc. Edinburgh. 1853.

[4] Jahresbericht. Wagner, 1858, p. 499.

Perhaps the nearest approach to a definition would be the following: Coal is a solid mineral substance, more or less easily combustible, varying in colour from dark brown to black, opaque—except in extremely thin slices—brittle, not fusible without decomposition, not sensibly soluble in ether, benzole, chloroform, or turpentine—not containing sufficient earthy matter to render it incapable of being applied with advantage as a source of heat in ordinary fire-places or in furnaces. This would exclude amber and other resinous matters, bitumen, and bituminous schists when they contain so large an amount of earthy matter as to be incapable of being employed as fuel; and, I think, it would also exclude even the most compact varieties of peat, none of which can be properly considered as brittle.

My friend Dr. Bennett has proposed a definition of coal founded on the appearance, under the microscope, of certain rings in a well-made transverse section; and he maintains that by means of this appearance all kinds of coal, whether household or cannel, can at once be distinguished from the Torbanehill mineral.[5] I do not, however, find that this distinction has been accepted by histologists. Dr. Bennett repudiates the verdict of the Scotch jury. He writes, "at the trial it was very plausibly argued that, in a bargain between man and man, scientific truths were of no value, and that a whale among whalers was still a fish. But as no naturalist, conversant with the structure and functions of a whale, would for a moment suppose it to be a fish because it inhabits the water and resembles one, so, I contend, no histologist acquainted with the structure and properties of the Torbanehill mineral ought to maintain that it is coal because it is dug out of the earth and burns in the fire."

Whatever difference of opinion there may be respecting the mode of accumulation of the great deposits of coal—whether these deposits have, like peat, been produced *in situ*, or whether they have been derived from drift-wood—there can be no doubt that coal, as has been previously stated, is the product of the decomposition of vegetable matter under special conditions. If we study the analyses of coals, we can readily select a series which illustrates the gradual passage of woody tissue into anthracite, or that variety of coal which consists almost wholly of carbon. Such a series is presented in the following tabular form, the proportion of carbon being estimated at the constant amount of 100.

	Carbon.	Hydrogen.	Oxygen.
1. Wood (from mean of analyses 1—26)	100	12·18	83·07
2. Peat	100	9·85	55·67
3. Lignite, average of 15 varieties	100	8·37	42·42
4. Ten-Yard coal of the South Staffordshire basin	100	6·12	21·23
5. Steam coal from the Tyne	100	5·91	18·32
6. Pentrefelin coal of South Wales	100	4·75	5·28
7. Anthracite from Pennsylvania, U. S.	100	2·84	1·74

[5] An investigation into the structure of the Torbanehill mineral and of various kinds of coal, by John Hughes Bennett, M.D., F.R.S.E. Trans. of the Royal Soc. of Edinburgh, v. 21, part 1, p. 173. 1854.

From this it will be perceived that through these various stages of conversion the proportion of carbon relatively increases while that of the hydrogen and oxygen decreases.

If we examine the relation between the hydrogen and oxygen in these successive degrees of conversion, we shall find that, with the exception of anthracite, there is a steady increase in the proportion of hydrogen beyond that required to form water with the oxygen present. The following numbers express this gradual increase in the excess of hydrogen.

	Hydrogen.		Hydrogen.
1.	1·80	5.	3·62
2.	2·89	6.	4·09
3.	3·07	7.	2·63
4.	3·47		

The formation of these products of the decomposition of woody tissue may be explained by the elimination of hydrogen in combination with carbon as *marsh-gas*, of oxygen in combination with carbon as *carbonic acid*, and of hydrogen in combination with oxygen as *water*.[6] That the derivation of coal from woody tissue has been accompanied with the evolution of marsh-gas might be inferred from the nature of the gases generally occurring in coal-mines, of which that gas is the chief constituent. However, the hydrogen and oxygen are never completely separated, as these elements are always present in sensible proportion in anthracite, which is furthest removed from woody tissue in composition.

Nitrogen is always found in coal, and its proportion seems to range pretty constantly between 1 and 2 per cent. Although nitrogen does not appear to be an essential element of woody tissue, yet that tissue is always associated with nitrogenous matters, so that the source of nitrogen in coal is readily accounted for. Hence ammonia is generated in the dry distillation of coal, and the product is, consequently, alkaline. In the dry distillation of woody tissue, on the contrary, the product is acid, owing to the presence of free acetic acid.

Sulphur is always present in coal. It may exist in the state of sulphuric acid in combination with a base; in combination with iron as iron pyrites or bisulphide of iron; and, probably, also in combination with the organic elements of coal as it exists in albumen. It chiefly occurs in the state of iron pyrites. In the dry distillation of coal a portion of it is evolved partly as sulphuretted hydrogen and partly as bisulphide of carbon.

All coal contains a greater or less proportion of water, which may be expelled at or slightly above 100° C. A coal may appear perfectly dry and yet lose by desiccation a very large amount of water; as much even as 20 per cent. Whether the water exists wholly as hygroscopic water, or whether, in some cases, it may not be partially combined, is doubtful; yet facts will be advanced in the sequel which seem to support the latter view. The amount of water which may re-

[6] Vid. Organic Chemistry in its applications to Agriculture and Physiology. Liebig. Trans., 1840, 327. Also, Lehrbuch der Chemisch. u. Physikalisch-Geologie. Bischof, 2. p. 1780.

main in some varieties of coal, even after desiccation by free exposure to the air, deserves more attention than it generally receives from metallurgists.

All coal contains a sensible amount of inorganic matter, of which the chief constituents are silica, alumina, lime, and iron. It is this matter which appears as the ashes of coals. Now, admitting that alumina is not an ordinary constituent of plants, it follows that the matter of which the ashes are composed has been derived, not merely from the inorganic elements originally existing in the plants from which coal has been produced, but also from an extraneous source. When we consider the conditions under which coal must have been formed, we can be at no loss to understand how such extraneous matter should have been deposited in a coal-field by the agency of water. We have only to inspect a coal-seam to have ocular and positive proof of the interstratification of coal and earthy matter such as shale and sandstone. In illustration we may take the familiar but extreme case of blackband ironstone. This ironstone consists essentially of carbonate of iron intimately mixed with coal. If further proof were needed of the admixture of coal with such extraneous matter, it is furnished conclusively by the results of Taylor, who has analysed the matter forming the bed and the roof of a coal-seam at Newcastle (*Buddle's Hartley* and Blaydon Burn Colliery), as well as the ashes of the intervening coal. The analyses are as follow:—[7]

	1.	2.	3.	4.	5.
Silica	62·44	59·56	64·21	56·51	58·99
Alumina	31·22	12·19	28·78	31·89	26·19
Sesquioxide of iron	2·26	15·96	2·27	..	5·14
Protoxide of iron	..	..	..	7 04	5·11
Lime	0·75	9·99	1·34	1·69	0·67
Magnesia	0·85	1·13	1·12	0·85	1·54
Potass	2·48	1·17	2·28	1·38	2·34
Soda	..	..	..	0·61	..
	100·00	100·00	100·00	99·97	99 98

1. *Fire-clay*, on which the coal rests, after subtraction of 10·5 per cent. of water and 0·44 per cent. of chloride of sodium and sulphate of soda. 2. Ashes of *good coal* (1·36 per cent.), after subtraction of 8·2 per cent. of sulphuric acid. The source of the sulphuric acid will be explained in the sequel. 3. Ashes of the *coarse coal* (16·9 per cent.), after subtraction of the sulphuric acid. 4. *Bituminous shale*, after subtraction of 39·35 per cent. of organic matter. 5. *Bluish shale*, after subtraction of 11 per cent. of water.

Ashes of coal.—In the choice of coal, attention should be directed to the *nature* as well as the *proportion* of the ashes which it may yield. The proportion may be so great as to lessen its value in a very material degree, or even to render it useless as a fuel for many purposes. It may be determined by incineration at a red heat in a platinum or porcelain crucible. The process may be conveniently conducted

7 Bischof, Lehrbuch der Chemisch. u. Physikal. Geologie, v. 2, p. 1771. Edinb. New Philos. Journ., 1851, v. 50, p. 140.

either over an air-gas flame or in a muffle. In respect to the *nature* of the ashes, the amount of oxide of iron is a point of chief importance. Iron pyrites is present in all coal, in which it may occur either invisibly diffused through the mass—in visible laminæ—or in layers and nodules, sometimes of considerable size. The spontaneous combustion of coal in coal-mines appears to be due, in part at least, if not wholly, to the heat developed by the oxidation of intermixed pyrites by atmospheric air. When some kinds of coal are left exposed to the air, yellow spots will eventually appear here and there on the surface, which consist of basic sulphate of sesquioxide of iron (misy) derived from the oxidation of pyrites. At first sulphate of protoxide is formed, of which the quantity is occasionally so great as to cause complete disintegration of the coal. The water which flows from coal-mines frequently contains in solution sufficient sulphate of iron to communicate a strong chalybeate taste. Such a solution rapidly corrodes iron boilers, and by free exposure to the atmosphere will deposit a yellow-brown ochreous compound of basic sulphate of sesquioxide of iron. Shale, which consists essentially of silicate of alumina, is generally present in coal in a greater or less degree, as will appear from the analyses of the ashes of coal, and when it is in contact with iron pyrites in process of oxidation by exposure to the air it may give rise to the formation of iron-alum in white asbestiform fibres. The formula of this beautiful substance is $FeO, SO^3 + Al^2O^3, 3SO^3 + 24HO$.[8]

The iron pyrites in coal will be represented in the ashes by an equivalent amount of sesquioxide of iron, provided incineration be perfect; and generally by far the greater portion of the oxide of iron in the ashes is derived from pyrites. The proportion of that oxide may be sufficient to give a red colour to the ashes, or it may not be sufficient to cause sensible coloration; hence the distinction between *red* and *white ash* coals. The intensity of the red colour, taken in connexion with the amount of ashes in coal, may serve as an indication of the proportion of sulphur existing in the state of pyrites. When a coal contains pyrites in considerable quantity, especially in the state of nodules, it may speedily destroy the fire-bars of a furnace. In one instance in which a highly pyritic coal was employed in a reverberatory furnace I observed ferruginous masses depending like stalactites from the lower surface of the bars, which were rapidly corroded in consequence. When the ashes sinter together or melt, they form a more or less vitrified mass termed *clinker*, which may accumulate upon the bars so as greatly to impede the passage of air between them, and, as a consequence, lower the temperature of the furnace. Moreover, when the bars are covered with a firmly-adherent bed of clinker, and are no longer cooled by a continuous current of cold air, they may soon become heated and destroyed by oxidation. Now the presence of much oxide of iron in the ashes may, in a certain degree, increase their fusibility, and so tend to induce the evil arising from the forma-

[8] Handwörterbuch des Chemisch. Theils der Mineralogie, Rammelsberg, part 1, p. 10, 1841. Outlines of Mineralogy, etc. Thomson, 1, p. 472. 1836. Berthier, Ann. d. Mines, 5, p. 259. 1820.

tion of an impervious bed of clinker. In this case a greater expenditure of manual labour would be required in removing clinkers, or, as it *is* termed, in *clinkering* the grate. But sometimes a bed of clinker is expressly formed, and made to serve an important purpose. Thus in furnaces in South Wales such a bed is ingeniously used as a substitute for a grate, on which small and inferior coal may be consumed which could not be otherwise profitably applied. The bed is allowed to become 12 or 20 inches thick, and requires to be supported only by a few bars, which, being far removed from the fuel, remain comparatively cool. It is kept broken up, so that a sufficient quantity of air may traverse it; and, in proportion as it accumulates above, it is cut away underneath by means of a crowbar with a cutting-edge and a heavy hammer. This operation is termed *breaking the grate*. However, as a rule, the less a coal clinkers the better for most purposes, and for none more so than boiler-furnaces. Irrespective of the formation of clinker, a certain amount of inorganic matter in coal is sometimes beneficial in preventing the fire from too rapidly collapsing, as it were, in the furnace. On this account a kind of coal called *brasils*, which occurs in the middle of the ten-yard coal in South Staffordshire, is preferred for reverberatory furnaces by some smelters in Birmingham.

Errors in analysis of coal.—When coal contains much inorganic matter, especially iron pyrites, the usual method of calculating its composition from the data obtained in the process of organic analysis may be erroneous in a sensible degree. The ashes left by incineration are estimated as inorganic matter, and the proportion of *oxygen* is found by subtracting the sum of the carbon, hydrogen, nitrogen, and ashes from the amount of dry coal subjected to analysis. By incineration the iron of the pyrites is converted into sesquioxide, and the sulphur, in a greater or less degree, into sulphuric acid, which may remain in combination with any base in the ashes—such as lime—capable of forming a sulphate not decomposable at a red-heat. Supposing the whole of the sulphuric acid to be thus retained in the ashes, for 1 part of iron pyrites there would be an increase of 1 due to oxygen derived from the air during incineration. The whole amount of this error, provided no correction be made, would fall upon the oxygen. It is not asserted that the whole of the sulphur is actually converted into sulphuric acid and retained in the ashes, but that a considerable portion of a stable sulphate may be produced during incineration will appear from analyses of coal in the sequel. It is certain that the alumina in the ashes must, in great measure, exist in combination with silica as clay; but clay holds water in combination which cannot be expelled except at a temperature far more than sufficient to decompose coal. Hence, during the process of organic analysis water may be evolved from the clay present in coal, and so occasion an error of excess in the determination of the hydrogen. This source of error has been pointed out by Regnault.[9] Carbonate of lime is sometimes present in coal in very appreciable quantity, in which case carbonic acid would be evolved during the analysis, and so an error of excess would

[9] Ann. des Mines, 3 s. 12, 167.

be caused in the determination of the carbon. M. de Marsilly has observed that, however pure a piece of coal may be, and however homogeneous it may appear to the eye, its different parts do not yield the same proportion of fixed residue by incineration; and the same is true in respect to the proportion of coke obtained by the calcination of different fragments of the same lump of coal. Hence, in every case, the proportion of ash and coke should be determined by operating upon an average sample taken from the powder of the coal.[1]

LIGNITES.—The synonyms are brown coal, bituminous wood, and pitchcoal of Werner (Pechkohle). Geologists apply the term lignite only to those carbonaceous minerals which occur in deposits of later date than the true coal-measures; and yet these minerals may occasionally not be distinguishable, either in physical characters or chemical composition, from undoubted bituminous coal. However, the cases in which lignites thus resemble bituminous coal are exceptional. Lignites seem generally to differ from other kinds of coal in the *large proportion of water* which they retain, even after free exposure to the atmosphere at the ordinary temperature. They appear to pass by insensible gradations into bituminous coal; and at present it seems impossible to construct a definition, except on geological grounds, which shall be characteristic of lignites alone, to the exclusion of all other kinds of coal. For the sake of convenience some varieties of coal which occur in formations posterior to the coal-measures, and which approximate closely to, if they are not identical with, certain kinds of bituminous coal, will be classed among the lignites proper. Moreover an illustration will thus be afforded that true coal, so far as relates to composition and external characters, is not confined to the coal-measures.

Lignite is either wood-like in structure, earthy, or compact; fracture conchoidal, wood-like, or uneven; colour of various shades of brown, brown-black, or black; lustre dull, shining or fatty; specific gravity generally ranges from 1·2 to 1·4; in composition it approaches nearer to wood than bituminous coal, and is specially distinguished from other kinds of coal in retaining a large proportion —from 15 to 20 per cent. or more—of water, even after desiccation by long and free exposure to the atmosphere at the ordinary temperature. Lignites are generally non-caking; that is, the powder of lignite when heated to redness in a close vessel does not yield a coherent coke. The term lignite is restricted by some persons to such varieties as manifestly present the appearance of woody tissue, the term *brown coal* being applied to all other varieties. Brown coal is the term at present used by the Germans as including all varieties, whether woody, earthy, or compact.

Classification of lignites according to external characters :—

a. *Pitchcoal* (Pechkohle, Glanzkohle).—Compact, occasionally cleaving into prismatic pieces; fracture conchoidal; pitch black; lustre waxy or fatty.

b. *Common brown coal.*—Compact; generally with slaty cleavage;

[1] Comptes Rendus, 1848, 46, 882.

wood-like structure indistinct; smooth conchoidal fracture; black-brown to pitch-black; lustre more or less glistening, or slightly fatty; of various shades of brown; lustre dull or glistening.

c. *Woody brown coal* (Bituminous wood). Massive, presenting the form and structure of wood.

d. *Schistose coal.*—Distinct slaty cleavage, sometimes separating into very thin leaves as in paper coal (Dysodil); occasionally sensibly elastic; brown.

e. *Earthy coal.*—Compact, but easily rubbed to powder; fracture earthy; dull; of various shades of brown.[2]

Composition of lignites.—We are indebted to Regnault for an excellent memoir on combustible minerals, published in 1837, from which the following instructive table is extracted. In this table is presented a series of analyses of lignites of tertiary origin, classified according to the degree in which their conversion from vegetable tissue has advanced.

TERTIARY LIGNITES.

Character of the Lignite.	Locality.	Nature of the Coke.	Specific Gravity.	Composition.				Composition after deduction of Ashes.			Coke per Cent.
				Carbon.	Hydrogen.	Oxygen and Nitrogen.	Ashes.	Carbon.	Hydrogen.	Oxygen and Nitrogen.	
1. Perfect lignite	1. Dax, south of France	Pulverulent	1·272	70·40	5·59	18·93	4·99	74·19	5·88	20·13	49·1
	2. Bouches-du-Rhône	do.	1·254	63·88	4·58	18·11	13·43	73·79	5·29	20·92	41·1
	3. Hesse-Cassel	do.	1·351	71·71	4·85	21·67	1·77	73·00	4·93	22·07	48·5
	4. Basses Alpes	do.	1·276	70·02	5·20	27·77	3·01	72·19	5·36	22·45	49·5
2. Imperfect lignite	5. Greece	Like wood charcoal	1·185	61·20	5·00	24·78	9·02	67·28	5·49	27·23	38·9
	6. Cologne		1·100	63·29	4·98	26·24	5·49	66·96	5·27	27·77	36·1
	7. Usnach (fossil wood)		1·167	56·04	5·70	36·07	2·19	57·29	5·83	36·88	..
3. Lignite passing into bitumen	8. Elbogen, Bohemia	Puffed out (bour-soufflé)	1·157	73·79	7·46	13·79	4·96	77·64	7·85	14·51	27·4
	9. Cuba	do.	1·197	75·85	7·25	12·96	3·94	78·96	7·55	13·49	39·0
Asphaltum	10. Mexico	. .	1·063	79·18	9·30	8·72	2·80	81·46	9·57	8·97	9·0

1. Fine black; powder brown; fracture uneven; but slight lustre; no ligneous texture; the particles keep their form and do not stick together or cake when heated. 2. Occurs in limestone; very schistose; pure black; powder brown; very brilliant; the texture of wood can no longer be recognised, except in less changed portions, which are brown; particles keep their form when heated, and do not cake; burns with a very brilliant and smoky flame. 3. Occurs in clay resting on Muschelkalk. The specimen analysed was extremely brilliant; fracture conchoidal; it resembles the finest jet, but is more tender; powder black-brown; the particles when heated stick a little together, but without fritting, *i. e.* forming a sensibly agglutinated mass. 4. Occurs in limestone; black; powder clear brown; lustre fatty; compact; coke slightly swelled out; it may be used in a smith's fire. 5. This lignite is worked on the banks of the river

[2] Vide Naumann, Elemente der Mineralogie, 1846, p. 426. Also Classification u. Beschreibung der Felsarten von F. Senft, 1857, p. 403.

Alpheus, in Elis, Greece. Foliated; laminæ thick; dull black; powder brown; presents much indication of vegetable structure, which in some pieces is perfectly preserved; the particles keep their form when heated. The portion analysed was treated with hydrochloric acid in order to remove carbonate of lime, of which it contained a large quantity. 6. Occurs in thick beds in sand and clay on the banks of the Rhine from Cologne to Bonn. Reddish brown; powder brown red; friable; ligneous texture very decided; gives a coke like wood charcoal.* 7. Occurs at Usnach, on the borders of the Lake of Zurich, Switzerland. Brown, almost black; powder clear brown; very hard and cannot be cut, yet with much trouble it can be pounded in a mortar; woody texture, still perfect. 8. Occurs as a thick bed in clay, and is used for firing porcelain. Blackish-brown; powder reddish-brown; compact; homogeneous like jet; fracture conchoidal, dull; yields a very light brilliant coke semi-metallic in lustre; contains 1·77 per cent. of nitrogen. 9. Velvety black colour; lustre very fatty; easily melts when heated, and leaves a very light puffed out coke. Regnault regards this mineral as forming the passage from lignites to bitumens or asphaltum. Geological position not certain, but presumed to be tertiary. 10. Black; powder black; very brilliant; emits a very strong and disagreeable odour; melts below 100° C. Its geological position is not known.

COMPOSITION OF LIGNITES DRIED AT 100° C. OR UPWARDS.

Number.	Locality.	Specific Gravity.	Carbon.	Hydrogen.	Oxygen.	Nitrogen.	Sulphur.	Ash °/₀.	Water °/₀.	Coke °/₀.	Exclusive of Sulphur* and Ash.		
											Carbon.	Hydrogen.	Oxygen, inclusive of nitrogen.
1	Bovey, Devonshire	1·129	66·31	5·63	22·86	0·57	2·36	2·27	34·66	30·79	67·85	5·75	23·39†
2	Oedenburg, Hungary	1·285	..	..	..	..	0·91	2·39	18·60	..	70·84	4·71	24·44
3	Do. do.	1·334	..	..	..	..	1·63	4·64	17·10	..	71·36	5·09	23·54
4	Bodoncspatak, do.	1·327	..	..	..	..	4·27	3·30	10·84	..	59·88	4·55	35·56
5	Palojta do.	1·256	..	..	..	..	2·59	1·41	11·07	..	70·40	5·73	23·87
6	Zsemle, Comorn, do.	1·317	..	..	..	..	0·57	4·35	12·60	59·55	71·89	4·79	23·31
7	Wildshut, Upper Austria	1·306	53·79	4·26	25·39	..	0·98	15·58	26·15	54·7	64·46	5·10	30·44
8	Thallern, Austria	1·413	49·58	3·84	22·68	..	4·56	19·34	22·53	63·7	65·15	5·05	29·80
9	Gloggnitz, do.	1·364	57·71	4·49	22·14	..	3·12	12·54	25·15	54·4	68·42	5·33	26·25
10	Schönfeld, Bohemia	..	61·20	5·17	21·28	..	..	12·35	21·2	..	69·82	5·90	21·28
11	Do. do.	..	..	..	..	..	..	8·65	..	..	70·80	5·81	23·39
12	Meissen, Saxony	..	58·90	5·36	21·03	..	6·61	7·50	..	..	68·58	6·24	25·18
13	Do. do.	..	62·18	5·47	18·05	..	9·30	5·00	..	..	72·56	6·38	21·06
14	Riestedt, Prussia	1·218	61·13	5·09	31·95	..	..	1·83	31·66	..	62·27	5·18	32·55
15	Löderburg, do.	1·219	55·30	4·90	31·95	..	..	7·85	49·50	..	60·01	5·31	31·68
16	Teuditz, do.	1·263	54·02	5·28	27·90	..	..	12·80	48·60	..	61·95	6·06	31·99
17	Do. do.	..	49·91	5·20	32·42	..	..	12·47	..	..	57·02	5·94	37·01
18	Brumby, do.	1·263	47·78	4·28	18·42	..	..	29·52	40·60	..	67·79	6·07	26·14
19	Frankfort-on-the Oder, do.	..	59·65	4·86	26·41	..	..	9·08	16·07	..	65·61	5·34	29·05
20	Wittenberg, do.	..	64·07	5·03	27·55	..	..	3·35	17·26	..	66·29	5·20	28·51
21	Zscherben	..	61·26	5·76	17·44	..	..	12·54	45·37	..	73·47	6·59	19·94
22	Tiflis, Georgia	..	63·34	5·67	27·93	..	..	3·04	..	..	65·31	5·85	28·81
23	Irkutsk, Siberia	..	47·46	4·56	33·02	..	..	14·95	..	..	55·81	5·36	38·83
24	Laubach, Hesse-Darmstadt	..	57·28	6·03	36·10	..	..	0·59	..	..	57·62	6·07	36·31
25	Near Cassel, Hesse-Cassel	..	62·60	5·02	26·52	..	..	5·86	..	..	66·49	5·33	28·28
26	Sipplingen, Lake Constance	..	..	..	..	..	..	5·50	..	..	61·96	3·48	31·56
27	Island of Sardinia	..	59 98	4·75	29·42	..	..	5·85	..	50·00	63·71	5·05	31·24
28	Brit. N. America, Prairies, east of Rocky Mountains	..	56·50	3·65	18·91	0 80	0·60	5·62	13·92	..	70·75	4·57	24·68
29		..	50·60	3·24	14·41	0·90	0·42	15·93	14·50	..	73·17	4·68	22·15

* Except when the sulphur is not given in the eighth column. † Exclusive of nitrogen.

1. Brown; structure fibrous and lamellar; becomes rotten by immersion in water; does not soil the fingers; coke has a semi-metallic lustre; does not swell, and cakes but slightly; ash bulky and red; copper and lead were detected in this coal; it evolves an extremely offensive odour on burning.[3] 2. Finely fibrous brown coal. 3. Not fibrous. 4. Pitch black; powder brown; lustre of fresh surface often vitreous; structure here and there wood-like; breaks in rhombic pieces. 5. Black brown to light brown; powder brown; woody structure distinct; hard and difficult to pulverise; it contains a peculiar resin. 6. Black; powder brown; lustre imperfectly fatty; fracture uneven, schistose, often conchoidal or rhombic; no trace of vegetable structure; resists exposure to the air.[4] 7. Wood-like; the coke was obtained by slow coking; by rapid coking the yield was from 2 to 3 per cent. less. The dry coal absorbed from the atmosphere 10·8 per cent. of water in 24 hours, that is, only 7·3 per cent. less than the total amount expelled by desiccation at 100° C.[5] 8. Black-brown; wood-like (brown coal). The dry coal absorbed from the atmosphere 12·7 per cent. of water in 24 hours.[6] 9. Wood-like; much fissured (brown coal). The dry coal absorbed from the atmosphere 15·9 per cent. of water in 24 hours.[7] 10. Brown coal.[8] 11. Dark black-brown (brown coal).[9] 12. Brown coal.[1] 13. "Black coal" (Schwarz-kohle). Black variety of brown coal.[2] 14. 15. 16. 18. Brown coal from the Prussian province of Saxony; 14. "Fossil wood," *i. e.* presenting wood-like structure; 15. Earthy; 16. and 18. Earthy. The specific gravity and water were determined with the coal fresh from the workings. *Colour of ash*—14. reddish-white; 15. yellow-brown; 16. greyish-white; 18. greyish white.[3] 17. Earthy; from the same locality as 16, but the analysis is by another operator.[4] 19. 20. and 21. Brown coal.[5] 22. 23. Brown coal.[6] 24. Wood-like. 25. Brown coal.[7] 26. Brown coal.[8] 27. Occurs, rather more than half a mile from the sea, at Goneza, province of Iglesias, to the west of Cagliari. An analysis was made at Turin by Abbene and Rossi, and the mineral was also examined at the École des Mines, Paris, and described as black coal, schistose and pyritic, yielding a pulverulent coke and very ferruginous ashes. Sir Roderick Murchison informs me that this mineral probably belongs to the true coal-measures, in which case it presents an interesting illustration of

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[3] 1. By F. Vaux, Journ. of Chem. Soc. London, v. 1. 318. 1849.

[4] 2 to 6. By Nendtwich, Chemisch-techn. Unters. d. vorzüglicheren Steinkohlen-Lager Ungarns. Von Prof. Nendtwich, (aus dem October-Hefte des Jahrganges 1851 der Sitzungsberichte der math-naturw. Classe der kaiserl. Akademie der Wissenschaften besonders abgedruckt.)

[5] 7. By Schrötter, Liebig u. Kopp, Jahresb. 1849, p. 708; Kenngott, 1853, p. 149.

[6] 8. Id. [7] 9. Id.

[8] 10. By Baer, Kenngott, 1853, p. 151.

[9] 11. By Köttig, Kenngott, 1852, p. 258.

[1] 12. By Grüger, Berzelius, Jahresber. 1848, p. 261.

[2] 13. Id.

[3] 14 to 16 and 18. By F. Bischof, manager of the salt-boiling works at Dürrenberg (Ober-siedemeister). Berg. u. H. Zeit. 1850, p. 69, quoted from Bergwerksfr. v. 13.

[4] 17. By Wagner, id., quoted from Polyt. Centralbl. 1847, p. 1496.

[5] 19 to 21. By Baer, Liebig u. Kopp, Jahresb., 1852, p. 733.

[6] 22, 23. By Woskressensky, Kenngott, 1852, p. 256.

[7] 24, 25. By J. von Liebig, Kenngott, 1852, p. 257.

[8] 26. By L. Gmelin, Kenngott, 1856, p. 117.

the fact that a coal of the coal-measures may remarkably resemble a true lignite in respect to composition.[g] 28, 29.[1] Brought by Dr. Hector. 28. Dark-brown, compact, in part wood-like and in part resembling coal of the coal-measures; fracture more or less conchoidal. 29. Cracked in small pieces during desiccation by exposure to the air. Much resembling coal of the coal-measures in appearance.

Mr. G. P. Wall, formerly a student of the School of Mines, in the course of a recent official survey of the geology of the island of Trinidad collected specimens of lignites which present many points of interest. They have been analysed in my laboratory by C. Tookey. The combustion was effected in a current of oxygen. The temperature at which desiccation was effected ranged from 100° to 110° C. The results are as follow:—

Composition inclusive of Hygroscopic Water.

	1.	2.	3.	4.
Hygroscopic water	20·50	5·90	16·80	17·65
Carbon	60·13	69·53	57·38	56·19
Hydrogen	4·14	5·36	3·74	4·14
Oxygen and nitrogen	10·77	15·22	17·50	17·39
Sulphur	2·36	0·55	0·68	2·23
Ash	2·10	3·44	3·90	2·40

Composition exclusive of Hygroscopic Water.

	1.	2.	3.	4.
Carbon	75·63	73·11	71·58	68·23
Hydrogen	5·20	5·63	4·66	5·02
Oxygen and nitrogen	13·57	17·08	18·09	21·14
Sulphur	2·96	0·57	0·84	2·70
Ash	2·64	3·61	4·86	2·91

No. 1. Black; fracture dull; powder brown; does not cake when heated in a close vessel; yields 43·15 per cent. of a non-coherent coke.

1. Combustion } Hydrogen per cent. { 5·26 } Carbon per cent. { 75·85
2. Do. } { 5·18 } { 75·65

No. 2. Black; bright, like good bituminous coal; friable; fracture uneven; powder dark brown. This variety scintillates much when held in a flame; when heated it evolves an odour like petroleum; cakes, and yields 54 per cent. of a firm, coherent coke; ash red.

1. Combustion } Hydrogen per cent. { 5 53 } Carbon per cent. { 73·95
2. Do. } { 5·84 } { 73·82

No. 3. Black; compact; fracture conchoidal and smooth; powder brown; does not cake; yields 51·8 per cent. of a non-coherent coke.

1. Combustion } Hydrogen per cent. { 4·91 } Carbon per cent. { 69·03
2. Do. } { 5·00 } { 69·14

No. 4. Black; compact; fracture uneven and dull; powder brown; does not cake; yields 44·95 per cent. of a non-coherent coke.

1. Combustion } Hydrogen per cent. { 5·01 } Carbon per cent. { 68·20
2. Do. } { 5·06 } { 68·33

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[g] 27. Ann. des Mines, 4. s. 20. p. 680. 1851.

[1] 28, 29. By C. Tookey, in my laboratory. 28. Saskatchewan Plains, La Roche Percée, Lat. 49° 7′ N., Long. 115° W. Tertiary (?). Specimen taken Aug. 1857; analysis made June 1861. 29. From 6 ft. seam, right bank of Saskatchewan, at Fort Edmonton, Lat. 53° 33′ N., Long. 113° 20′ W. Lower cretaceous (?).

On inspecting the preceding analyses of lignites it will be observed that, with the exception of No. 2 of the Trinidad specimens, all contain a *large proportion of water*, a proportion far exceeding that which is found in any coals of the coal-measures. No. 2 presents an example of a lignite which, on the ground of physical character and chemical composition, should be classed as a bituminous coal of the coal-measures.

Lignites from Auckland (New Zealand) and Tasmania have also been analysed in my laboratory by C. Tookey. The results are as follow:—

	1.	2.
Hygroscopic water	14·12	13·43
Carbon	55·57	59·90
Hydrogen	4 13	4·66
Oxygen	15·67	15·99
Nitrogen	1·15	1·08
Sulphur	0·36	0·30
Ash	9·00	4·64

No. 1. From Auckland; black; lustre dull; fracture uneven, more or less conchoidal; distinct cleavage; shining, more or less transparent; brown resin occurs diffused through this lignite in pieces varying in size from a pea to considerable masses. Two combustions were made. In the first the hydrogen was 4·07 and the carbon 55·65 per cent., and in the second the hydrogen was 4·18 and the carbon 55·48 per cent. No. 2. From Tasmania. The specimen was sent by Governor Denison. In physical characters it was similar to the last described, and it also contained resin diffused in like manner through its substance. Accompanying the specimen of lignite was a piece of resin as large as the fist, which was more opaque, and less resembling ordinary varieties of amber in appearance, than that of No. 1. By the action of benzole a portion only dissolves; a gum-like insoluble mass is left, which retains the form and bulk of the original resin.

Composition of the ashes of lignite.—The following analyses by Kremers will suffice for illustration:—[2]

	1.	2.	3.	4.
Silica	15·48	45·13	60·23	31·30
Sesquioxide of iron	74·02	25·83	6·36	54·47
Alumina	5·28	22·47	31·63	8·31
Lime	2·26	2·80	1·08	3·44
Magnesia	0·26	0·52	0·35	1·60
Potash	0·53	0·80	0·11	0·07
Soda	...	0·28	...	0·29
Sulphuric acid	2·17	2·37	0·24	0·52
	101·53	101·60	98·37	98·95
Ash per cent.	1·99	1·89	1·74	11·18

1. From Oberndorf. 2 and 3. From Zwickau, Saxony. 4. Waldenburg, Silesia.

[2] De relatione inter carbones fuscos atque nigros. Dissert. Inaug. Auctor Petrus Kremers. Berolini. 1851.

Daubrée has detected arsenic in the lignite of the tertiary strata at Lobsann, Lower Rhine. Ordinary specimens of this fuel contained from 0·002 to 0·0008 of their weight of arsenic.[3]

Bituminous Coals.—This term is commonly applied to coals from the coal-measures which, under ordinary conditions, burn with a more or less smoky flame. In respect to the degree in which they are removed from woody tissue in chemical composition, they occupy a position between lignites on the one hand and anthracites on the other. The passage of lignite into bituminous coal is as gradual as the passage of bituminous coal into anthracite, so that there is no precise line of demarcation between coals of this class and those of the other two classes. Hence it may well be conceived that in the class of bituminous coals many varieties of coal must be included which in external characters and composition present considerable diversity. The mineral *bitumen* burns with a smoky flame, and on this account coals which burn in a similar manner have been characterised as *bituminous*. This application of the term has occasionally led to the erroneous notion that bituminous coals necessarily contain a substance similar to bitumen. Natural bitumen readily dissolves in solvents such as ether or benzole, but no sensible amount of matter can be extracted from ordinary bituminous coals by these solvents. By some writers the term bituminous is used to denote the matter which is *volatilised* when a coal is heated, at least to redness, in a close vessel, in which sense it is synonymous with *volatile matter*, both terms being employed indiscriminately. By other writers it has been used to express the so-called *organic* elements of coal other than carbon, namely, hydrogen, oxygen, and nitrogen.

The characters of bituminous coals may be summed up as follows:—solid, brittle, opaque; lustre dull, shining, or fatty; colour black or brown-black; colour of the fine powder brown or brown-black; some soil the fingers, and others do not; hardness variable; fracture even, conchoidal, or uneven; they frequently break into pieces more or less cubical or rhombic; they present no definite signs of crystallization; they consist of carbon, hydrogen, oxygen, nitrogen, and sulphur, and of fixed or inorganic matter; they burn with a more or less smoky flame, and when heated in a close vessel leave a solid carbonaceous residuum termed coke, which contains the fixed inorganic matter or ashes.

Caking coal.—When some coals of this class are heated to a certain degree they swell, become pasty, and more or less fused, emitting bubbles of gas, which burn with a bright flame as they escape. If the powder of such coals is thus heated to the pasty state the particles stick together and form a coherent mass, or, in technical language, the coal is said to *cake*. When coal in the pasty state is taken out of a fire it remains for a short time soft and dough-like, but on cooling it becomes solid and brittle. In the quality of caking there may be

[3] Ann. d. Mines, 5. s. 14. p. 472. 1858.

every degree, from slight fritting or sintering to almost complete fusion. Caking does not occur at a temperature below that at which the coal suffers decomposition, so that it is not due to the soldering of the particles together by mere fusion, as would occur with particles of wax by exposure to a gentle heat. The mode in which a coherent coke may be conceived to be produced may be illustrated by the following experiment. When the powder of charcoal or anthracite is heated in a covered crucible, even after having been well rammed in, no degree of caking will take place under any conditions of temperature; but if the powder be mixed with a little coal-tar or coal-tar pitch, and afterwards similarly heated, a firmly caked or coherent mass may be obtained, which may be thus made so solid and hard as to give a sonorous ring when struck. The tar or pitch is decomposed when sufficiently heated in a close vessel and resolved into *volatile products* and a *fixed residuum* of shining carbonaceous matter; and it is this matter which acts the part of a solder and binds firmly together the particles of charcoal or anthracite. Now in the case of caking coals at a certain degree of heat, products appear to be formed which are subsequently resolved, at a higher temperature, into volatile matter and a carbonaceous residuum, and so a coherent coke is produced. Of the nature of these products I am not aware that we have at present any certain knowledge.

It is interesting to inquire whether the caking quality depends simply on the *elementary* composition of a coal irrespective of its *proximate* constitution. It is obvious that this question would be immediately solved if it could be shown that a *caking* and *non-caking* coal may have the same elementary or ultimate composition. Mr. Nicholas Wood, so well known in connexion with the coal-trade of the Tyne, obligingly supplied the author with samples of two kinds of coal from the vicinity of Newcastle, which, he believed, had the same elementary composition, but of which one was caking and the other non-caking. These coals were carefully examined and analysed by Mr. Dick in the metallurgical laboratory of the School of Mines, and the result was, that although their elementary composition was very similar, it was yet far from identical, and that both caked, though in a different degree.

If we inspect the following table, in which is presented the composition of a series of coals, caking and non-caking, we shall be disposed to suspect that there might be an essential connexion between the caking quality and elementary composition. In order to be able to compare these coals with each other, the hydrogen and oxygen, inclusive of nitrogen, are calculated in relation to the constant quantity of 100 of carbon.

	1.	2.	3.	4.	5.	6.	7.	8.	9.
Carbon	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·0
Hydrogen ...	4·75	4·45	5·49	5·85	5·91	6·34	6·12	6·04	5·9
Oxygen and nitrogen .	5·28	7·36	10·86	14·52	18·07	21·15	21·23	22·55	23·4
	Non-caking.		Caking.			Non-caking.			

The excess of hydrogen in these nine varieties of coal above that required to form water with the oxygen will be respectively—

4·09 4·53 4·13 4·04 3·65 3·70 3·47 3·22 3·06

These numbers are erroneous to the extent of the nitrogen, which in the calculation has been included in the oxygen, but the amount of error arising from this cause may be disregarded.

Hence it would seem that no essential relation exists between the excess of hydrogen and the property of caking, for that excess is nearly identical in Nos. 1 and 4, which are non-caking and caking respectively. If we now estimate the sum of the hydrogen and oxygen existing in each of these coals we obtain the following results :—

10·03 11·81 16·35 20·37 23·98 27·49 27·35 28·59 29·41

We might, therefore, be led to infer from the preceding data that the property of caking is connected essentially with the proportion of oxygen, and that when the oxygen in a coal exceeds in round numbers 7 per cent., and does not exceed 18 per cent., the coal would have the property of caking. This inference, however, in respect to general application, is entirely opposed to the researches of Stein, Professor of Chemistry at the Polytechnic School of Dresden, to whom we are indebted for a monograph on the coals of Saxony.[4] I have selected from this monograph the following series of results, which would appear to establish the fact that caking and non-caking coals may have the same ultimate composition.

STEIN'S TABLE.

Number.	Locality.	Specific Gravity.	Carbon.	Hydrogen.	Oxygen.	Nitrogen.	Sulphur.	Ash.	Coal air-dried. Water per Cent.	Composition exclusive of Ash. Carbon.	Hydrogen.	Oxygen.	Nitrogen.	Coke exclusive of Ash.	Result of Coking.
1	Oberhohndorf	1·266	82·42	4·50	11·61	0·43	1·21	0·74	4·75	83·28	4·55	11·73	0·44	47·70	Caking.
2	Zwickau	1·300	80·25	4·01	10·98	0·49	2·99	1·57	5·91	83·82	4·19	11·47	0·51	69·59	Coke described as like the coal itself, so that not even fritting could have occurred.
3	Do.	1·298	76·59	4·12	12·87	0·33	0·81	6·00	5·07	81·47	4·38	13·71	0·35	54·64	Caking.
4	Niederwürschnitz ..	1·378	72·35	4·17	11·99	0·62	2·65	8·33	7·15	81·17	4·67	13·47	0·68	69·73	Coke crumbly.
5	Do.	1·311	80·49	4·10	10·62	0·20	1·10	3 64	9·11	84·36	4·30	11·13	0·21	62·40	Coke slightly fritted.
6	Planitz	1·280	81·23	4·43	9·86	0·21	0·55	4·25	4·85	84·84	4·63	10·74	0·23	63·89	Caking.
7	Niederwürschnitz ...	1·454	77·42	4·65	11·73	0·23	1·68	4·93	7·53	82·34	4·73	12·69	0·24	66·43	Coke sandy.
8	Zwickau	1·275	72·27	4·16	10·73	0·34	0·88	12·50	5·08	82·59	4·76	12·26	0·39	77·29	Caking.
9	Do.	1·291	75·26	4·08	16·07	0·20	1·71	3·07	6·30	78·71	4·27	16·81	0·21	77·44	Caking.
10	Niederwürschnitz ..	1·331	76·03	4·35	16·05	0·13	0·13	3 31	8·48	78·74	4·51	16·62	0·13	60·81	Coke crumbly.

If we admit the fact that a caking and non-caking coal may have the same *ultimate* composition, we should be necessarily led to the conclusion that the quality of caking depends upon *proximate* constitution, that is, upon the *manner* in which the elements are combined. But we must

[4] Chemische u. chemisch-technische Untersuchung der Steinkohlen Sachsens. W. Stein. 1857.

wait for future information on this interesting subject, which seems well worthy of investigation.

As the passage of woody tissue into bituminous coal and of bituminous coal into anthracite is gradual, and as neither woody tissue nor anthracite is in the least degree caking, it follows that, beyond a certain limit—as a coal approximates in composition to woody tissue on the one hand and to anthracite on the other—the presence or absence of the caking property may be certainly predicated from ultimate composition alone.

It is asserted that some coals speedily lose the property of caking after having been drawn from the pit; and the author has it on good authority that a variety of coal which occurs at Penclawdd, near Swansea, loses its property of caking after exposure to the atmosphere not longer than one or two days. In this case the cause of the loss of the caking quality will probably be found to depend on the escape of something from the coal, or on the oxidizing action of the atmosphere upon the coal.

M. de Marsilly states that strongly caking coal, which yielded an excellent coke when fresh from the pit, yielded only an imperfectly formed coke in the same ovens after having been exposed to the air during six months.[5]

To the same observer we owe some interesting and important observations, which may throw light on the cause of the property of caking. He asserts that all caking coals (houilles grasses) from pits in which fire-damp occurs cease to swell up and cake when they have been previously heated to 300° C.; so that when they are calcined in the state of powder after having been thus heated they will be found in the state of powder after the calcination. I have confirmed the correctness of this assertion with respect to the strongly caking coal of Newcastle-on-Tyne. The powder of this coal was heated in the hot-air bath at a temperature ranging between 300° C. and about 304° C. It may be thus heated for about a quarter of an hour or so without sensibly losing its property of swelling up and caking; but when it is kept exposed to this temperature during one or two hours it does not swell up on subsequent calcination, and yields only a very slightly fritted coke. M. de Marsilly infers that the loss of the caking property by exposure to the air during a long time, and to the action of heat under 330° C. during a short time, is due to the same cause—the volatilization of matter upon which, he believes, the property of caking depends. Whether the loss of this property by long exposure to the air is due solely to the cause in question does not appear to be established.

The most important results of M. de Marsilly's investigation are the following:—1. The loss of weight which coal suffers by desiccation in vacuo is always less than that which is occasioned by exposure to 100° C. At 50° C. gas begins to be evolved from coal, but the evolution only becomes very sensible at 100° and upwards. It goes on increasing to 330°, when, probably, the decomposition, properly so called,

[5] Comptes Rendus, 1858, 46. 882.

of coal commences. The amount of gas evolved varies from 1 to 2 litres per kilogramme of coal (61 to 122 cubic inches per 2¼ lbs. avoird. nearly); and there is also distilled a liquid product, having the odour of benzine, of which the weight varies from 10 to 15 grammes per kilogramme of coal (154 to 231 grains per 2¼ lbs.). The loss in weight which coal undergoes at 300°, owing to the separation of gas and liquid combined, ranges from 1 to 2 per cent. 2. It is a remarkable fact that from the coal of pits subject to fire-damp, carburetted hydrogen is always and almost exclusively disengaged, whereas the gas evolved from the coal of pits free from fire-damp consists chiefly of nitrogen and carbonic acid without any trace of carburetted hydrogen. 3. Carburetted hydrogen is spontaneously evolved from coal newly won, even under a pressure five times as great as that of the atmosphere. After having been exposed to the air during six months—or probably less—coal yields no gas, not even at 300°. Hence M. de Marsilly is disposed to conclude that the gases disengaged by the free exposure of coal to the atmosphere are the same as those obtained by its exposure to 300°. This, however, is a conclusion which nothing short of analysis can justify.

In some instances the caking of a coal depends on the manner in which it is heated and the degree of heat to which it is subjected. Thus the South Staffordshire coals (Nos. 27-30 in the Table, p. 102) are practically non-caking coals; that is, the powder of these coals when heated in the usual way does not yield a coherent coke, but only a very slightly fritted and crumbling mass. Yet if it be *rapidly* exposed to a *high* temperature, such as a bright red heat, in a *close* vessel, a good solid coke may be obtained. There is an enormous amount of the slack of such coals annually raised in South Staffordshire, and an enormous amount also left under ground, which might be turned to a profitable account if coking, under the special conditions just mentioned, could be economically conducted.[6]

The amount of water in coal is not without influence on the property of caking, as will appear in the sequel.

When the proportion of inorganic matter in coal is very large, its influence in diminishing, if not in destroying the caking quality may be readily understood. However, according to Stein, a coal may yield as much as 21·67 per cent. of ashes and yet be caking.[7]

The property of caking may be very important in respect to the application of coal as a fuel, especially in metallurgical operations. Strongly caking coal may soon become agglomerated in the furnace into a mass so compact as to be, in a greater or less degree, impervious to air, in which case the fire, without stirring, would speedily be extinguished, and stirring, in many cases, would be quite impracticable. In the copper-furnaces at Swansea caking and non-caking—in other words, *binding* and *free-burning*—coal are used in admixture with

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[6] This is a subject affecting not merely South Staffordshire. According to Mr. Nicholas Wood "the waste at the Hetton and Black Boy Collieries alone amounted to 160,000 tons of small coal in a year."—*Colliery Guardian, July* 6, 1861.

[7] Op. cit. p. 93, Nos. 5 and 6 in the Table.

great advantage, the non-caking coal serving effectually to keep the fire *open* to the passage of air. Some kinds of coal possess the quality of caking in so high a degree as to stick firmly to the bars of a furnace, and cannot, therefore, be advantageously used even under steam-boilers.

Free-burning Coal.—This term is applied to coal which does not, in burning, sinter together, or cake, in a sensible degree. The fire remains open, so that the air can pass freely through it; whereas the reverse is the case with caking coal, which cannot, without admixture with free-burning coal, be directly applied in various metallurgical operations.

Cannel Coal.—This coal burns readily without melting, and emits a bright flame. A piece of good cannel coal when ignited will continue to burn for some time afterwards. The term cannel—a corruption of candle—is applied to coals of this kind because they burn like a candle. They are brown, brown-black, or black; fracture uneven or largely conchoidal; some are comparatively tough; others as brittle as other kinds of coal; they do not soil the fingers; some are susceptible of a fine polish, and may be wrought into articles of ornament. Thus jet is a variety of cannel coal. The term "Parrot" is applied to a cannel coal occurring near Edinburgh, on account of its burning with a crackling noise; and a variety of cannel coal from South Wales is termed "Horn Coal," because it emits while burning an odour like that of burning horn. Cannel coal is especially valuable as a gas-coal.

ANTHRACITE.—This coal is the ultimate product of the conversion of vegetable matter into coal. It generally contains upwards of 90 per cent. of carbon. The external characters by which anthracite is distinguished are as follow:—very compact; deep black; lustre bright, occasionally somewhat bronze-like or semi-metallic; brittle; fracture uneven or conchoidal; does not soil the fingers; burns with a feebly luminous, smokeless flame, and is much less combustible than other kinds of coal; when heated does not in the least degree sinter, but frequently decrepitates considerably.

Fibrous and granular matter in coals.—In some kinds of coal may often be observed thin layers or patches of black, fibrous, soft matter, which soils the fingers, and is much like wood-charcoal in appearance. It is met with in cannel coal, but in less quantity than in other bituminous coals. Under the microscope it is found to possess the structure of woody tissue.[6] A granular and more or less pulverulent variety of this matter also occurs in coals. Dr. Rowney has examined both kinds, and finds them to differ sensibly in composition from the coal with which they are associated. Both kinds exist in coal of the carboniferous series, but only the fibrous kind is mentioned as present in coal of the oolitic and tertiary formations. Rowney describes the pulverulent kind as occurring sometimes as a light powder, and at others as a cindery substance which peels off the coal in flakes easily reducible to powder.

[6] Dr. Bennett, Trans. of the Royal Soc. of Edinburgh, 1854, v. 2, p. 186.

Composition of Fibrous and Granular Matter in Coals, dried at 100° C.

	Character.	Carbon.	Hydrogen.	Oxygen.	Nitrogen.	Ash.
1.	Fibrous	82·97	3·34	6·84	0·75	6·08
2.	Granular	72·74	2·34	5·83		19·08
3.	Fibrous	73·42	2·94	8·25		15·39
4.	Do.	74·71	2·74	7·67		14·86
5.	Do.	81·17	3·84	14·98		

1. From the common household coals of the Glasgow coal-fields. 2. From the Stonelaws coals. 3. From Ayrshire coal. 4. From the Elgin splint coal, Fifeshire. 5. From the 5 feet seam, Elgin coal, Fifeshire.[7] The composition of the coals from which Nos. 3, 4, and 5 were taken, as determined by Rowney, will be found in Table, p. 102, Nos. 37–39.

Composition of the coals used in copper-smelting.—It has been previously stated (p. 84) that in the smelting-works of Swansea and the neighbourhood the clinker is allowed to accumulate to such an extent as to form a bed of considerable thickness, and that upon this bed, which is kept sufficiently open to allow of the passage through it of the proper amount of air to sustain combustion, small coal may be effectually burned which would in great measure drop through an ordinary grate composed of bars arranged in the same plane. It is requisite, therefore, that the inorganic matter of the coals employed should, at the temperature of the furnace, sinter or fuse together so as to form a solid coherent clinker, but that it should not run into an easily fusible vitrified mass. Being desirous of ascertaining the composition of the ashes of the coals which produce a suitable clinker, I applied to Mr. William Morgan for average samples of the coals which are consumed at the Hafod Copper-Works, of which he directs the smelting department. The samples were promptly supplied, and I have much pleasure in acknowledging the willing assistance which I have at all times received from Mr. Morgan, especially during the lifetime of the late Mr. Vivian—a man who was ever ready to aid the scientific inquirer, who made no pretension to the exclusive possession of mysteries, and whose memory is deservedly revered by the inhabitants of Swansea.

Three kinds of coal are used in admixture at the Hafod Works: one *binding*, or caking; and two *free-burning*, or non-caking. The mixture consists of the same weight of each of these three coals, viz., 1 part of Mynydd Newydd, or binding coal; 1 of Tyrcenol and 1 of Pentrefelin, or free-burning coals. The analyses have been made in my laboratory by my friend Mr. Dick. The ashes of each of these coals were exposed separately to a high temperature, and found to have about the same degree of fusibility.

[7] Edinb. New Phil. Jour., 1855, v. 2, p. 141.

Composition of the Ashes.

	1.	2.	3.
Silica	35·05	35·01	36·15
Alumina	26·00	28·01	28·12
Sesquioxide of iron	19·56	19·06	26·26
Lime	5·80	4·53	2·28
Magnesia	1·95	2·14	1·68
Potass	2·55	2·95	1·36
Soda	0·65	0·95	0·64
Sulphuric acid	8·45	7·14	3·17
	100·01	99·82	99·66

1. Mynydd Newydd. 2. Tyrcenol. 3. Pentrefelin. The ash of each coal was reddish, and that of No. 3 most so. The *total sulphur* in each coal was determined by deflagration in a gold crucible, with a mixture of nitre and chloride of sodium; and the *sulphuric acid pre-existing* in the coal in the state of sulphate was determined by digesting the powder of the coal in hydrochloric acid, and proceeding by the addition of a baryta-salt in the usual way. The greater part of the sulphuric acid in the ashes is the product of oxidation during incineration in the presence of strong bases. If we estimate the sulphur—exclusive of that in the sulphuric acid pre-existing in the coal—in combination with iron as iron-pyrites, the complete analyses of these coals will be as follow:—

		1.	2.	3.
Carbon		73·87	76·81	78·49
Hydrogen		3·73	3·42	3·73
Oxygen and nitrogen		8·02	5·65	4·15
Silica		5·05	4·68	4·24
Alumina		3·75	3·74	3·29
Sesquioxide of iron		0·88	0·10	0·00
Lime		0·83	0·60	0·27
Magnesia		0·28	0·28	0·19
Potash		0·36	0·39	0·16
Soda		0·09	0·12	0·07
Sulphuric acid		0·23	0·54	0·69
Iron-pyrites	Iron	1·36	1·71	2·16
	Sulphur	1·55	1·96	2·56
		100·00	100·00	100·00
Ash obtained by incineration, per cent.	1.	13·39	14·35	11·76
	2.	13·34	14·32	11·71
Mean		13·37	14·34	11·73

The iron introduced in the foregoing analyses is estimated as sesquioxide, a portion of which only, probably, existed in combination with the shale or clay, which was evidently present in very appreciable quantity.

Le Play has published the following analysis of clinker, reputed of good quality, which, if I mistake not, was procured at the Hafod Works.[1]

[1] Description des Procédés Métallurgiques employés dans le Pays de Galles pour la Fabrication du Cuivre. Paris, 1848, p. 122.

		Supposed mode of Combination.	
Silica	52·0	Silicate of sesquioxide of iron	11·0
Sesquioxide of iron	5·2	,, protoxide of iron	40·4
Protoxide of iron	22·0	,, of the earthy bases	45·1
Alumina	14·2	Sulphide of iron (FeS)	2·3
Lime	2·4	Carbon	1·2
Magnesia	0·7		100·0
Sulphur	1·3		
Iron	1·0		
Carbon	1·2		
	100·0		

These results do not closely accord with those obtained by Mr. Dick. Le Play makes no mention of potass and soda, which are certainly present in the ashes of the coals supplied by Mr. Morgan. Reasons will be given in the sequel which render doubtful the existence of silicate of sesquioxide of iron in the clinker.

Composition of Bituminous Coals.—In the following tables is presented a selection of analyses of British and foreign bituminous coals and anthracites. In a subsequent part of this work will be found analyses of certain coals of special interest in the smelting of iron in particular localities.

BRITISH CAKING COALS.

Number.	Locality.	Specific Gravity.	Carbon.	Hydrogen.	Oxygen.	Nitrogen.	Sulphur.	Ash %.	Water %.	Coke %.	Exclusive of Ash. Carbon.	Hydrogen.	Oxygen.	Nitrogen.*
1	Northumberland ..	..	78·65	4·65	14·21	..	0·55	2·49	..	..	80·54	4·76	14·70	..
2	Ditto ..	..	82·42	4·82	11·97	..	0·86	0·79	..	..	83·73	4·90	11·37	..
3	Ditto ..	1·276	81·41	5·83	7·90	2·05	0·74	2·07	1·35	66·7	83·26	5·65	8·22	2·87
4	Ditto ..	1·259	78·69	6·00	10·07	2·37	1·51	1·36	..	..	81·01	6·17	10·38	2·44
5	Nottinghamshire ..	..	77·40	4·96	7·77	1·55	0·92	3·90	3·50	63·18	84·43	5·41	8·47	1·69
6	Blaina, South Wales	..	82·56	5·36	8·22	1·65	0·75	1·46	..	..	84·42	5·48	8·40	1·70
7	Ditto ..	..	83·44	5·71	5·93	1·66	0·81	2·45	..	..	86·25	5·90	6·13	1·72
8	Ditto ..	..	83·00	6·18	4·58	1·49	0·75	4·00	..	..	87·14	6·49	4·81	1·56

* Where no figures are given under this column, the Nitrogen is included in the Oxygen.

1.[2] Sent by Mr. Nicholas Wood. The "Seaton Burn Steam-coal;" it is from the same bed as all the Hartleys, viz., West Hartley, Buddle's Hartley, &c. The powder swells up slightly when heated to redness, and *forms a coke.* In burning, this coal does not stick to the bars like No. 2, and it is therefore styled "open burning;" but this term is only correct when used comparatively with a coal like No. 2. An average sample for analysis was obtained from a large lump. In the table no correction has been made, the number under the column of Oxygen being found by subtracting the sum of the carbon, hydrogen, and ash (as left by incineration) from 100. The 2·49 of ash contained 0·49 of sulphuric acid (= 0·19 sulphur), and 0·39 of sesquioxide of iron (= 0·273 iron). But this quantity of iron requires 0·31 of

[2] By Dick in my laboratory.

sulphur to form pyrites. The excess of sulphur, therefore, beyond what was thus required, is $0{\cdot}55 - 0{\cdot}31 = 0{\cdot}24$.

2.[3] Also from Mr. Wood. The "Peareth Gas-Coal." It is of the quality called gas-coals, and is the same as the Pelow Main, Felling, Peltree, and other coals of the Tyne. The powder swells up when heated to redness, and forms a *coherent coke*. 0·74 of ash contained 0·06 of sulphuric acid. The ash had a reddish grey but lighter colour than that of No. 1. But if the ash had consisted entirely of sesquioxide of iron, there would not have been sufficient iron to form pyrites with all the sulphur present. Neither No. 1 nor 2 contained any appreciable amount of carbonate. Mr. Wood remarks that "it is curious that both these coals are from the same bed; but steam-coal exists north of Newcastle, and the gas-coal south of it, the change taking place nearly in the line of the river, and within a zone of three miles on the north side."

3.[4] Name of the seam not stated. The *coke caked together*, swelling considerably. Pyrites was visibly present in this coal.

4.[5] Fracture conchoidal; interspersed rather abundantly with iron pyrites; chiefly used for steam purposes, for which it is largely exported. From the "Low Main Seam," Buddle's Hartley Colliery.

5.[6] From Shireoak Colliery, belonging to the Duke of Newcastle. Ash bulky, and slightly pink in colour.

6.[7] Ell-vein coal. 7. Three-quarter-vein. 8. Big-vein. Mr. Adams, of the Ebbw Vale Iron-Works, which are situated in a valley adjoining and parallel to that in which are the Blaina Iron-Works, informs me that the Ell-vein and Big-vein are steam-coals with a white ash; and that the three-quarter coal is a furnace-coal.

FOREIGN CAKING COALS.

Number.	Locality.	Specific Gravity.	Carbon.	Hydrogen.	Oxygen.	Nitrogen.	Sulphur.	Ash °/₀.	Water °/₀.	Coke °/₀.	Exclusive of Ash. Carbon.	Hydrogen.	Oxygen.	Nitrogen.
9	Epinac	1·353	81·12	5·10	11·25	..	..	2·53	..	63·6	83·22	5·23	11·55	..
10	Alais, dép. du Gard	1·322	89·27	4·85	4·47	..	..	1·41	..	78·0	90·55	4·92	4·53	..
11	Rive-de-Gier ..	1·298	87·45	5·14	3·93	1·70	..	1·78	..	68·0	89·04	5·23	5·73	..
12	Ditto ..	1·288	82·04	5·22	9·12	..	..	3·57	..	72·0	85·08	5·46	9·46	..
13	Céral, dép. de l'Aveyron	1·294	75·38	4·74	9·02	..	..	10·86	..	58·4	84·56	5·32	10·12	..
14	Saint-Girons ..	1·316	72·94	5·45	17·53	..	..	4·08	..	44·8	76·05	5·69	18·26	..
15	Mons	..	85·10	5·49	7·25	..	..	2·16	..	72·90	86·08	5·61	7·41	..
16	Ditto	..	80·55	5·53	9·52	..	..	4·40	..	69·15	84·26	5·78	9·96	..
17	Ditto	..	86·38	4·48	6·09	..	..	3·05	..	80·58	89·10	4·62	6·28	..
18	Charleroi	..	86·47	4·68	5·30	..	..	3·55	..	84·43	89·65	4·85	5·50	..
19	Valenciennes ..	..	84·84	5·53	6·83	..	..	2·80	..	67·75	87·28	5·69	7·03	..
20	Pas-de-Calais ..	..	86·78	4·98	5·84	..	..	2·40	..	77·05	88·91	5·10	5·99	..
21	Hungary	1·295	•.	..	..	..	0·86	0·89	1·20	78·85	88·72	4·66	6·61	..
22	Ditto	1·300	..	..	..	..	0·99	2·85	1·14	83·14	88·85	4·23	6·92	..
23	Ditto	1·313	..	..	..	..	2·83	5 82	1·04	82·82	88·30	4·80	6·90	..
24	Ditto	1·378	..	..	..	..	5·53	11·41	1·57	77·81	83·76	4·97	11·26	..
25	Ditto	1·350	..	..	..	..	0·90	10·33	1·08	81·55	89·69	5·03	5·27	..
26	New Zealand ..	..	79·00	5·35	7·71	0·89	2·50	3·50	1·05	64·32	84·90	5·75	8·29	0·96

[3] By Dick. [4] By Vaux, op. cit. [5] 4. By Taylor, Ed. New Philos. Jour. v. 50. p. 142. [6] 5. By C. Tookey, in my laboratory. [7] 6–8. By Dr. Noad, and communicated by him to the author.

9.[8] Powder brown. Falls to pieces by exposure to the air, in consequence of the pyrites which it contains. It does not increase in volume by calcination; coke semi-metallic in lustre and *agglutinated*, but the different pieces from which it has been formed may be easily recognised.

10.[9] Powder black brown. Coke semi-metallic in lustre, *slightly* puffed up; the pieces from which it has been derived can often be distinguished. The coal is regarded as very hard, *i.e.* difficult to burn, but capable of producing a very high temperature. The coke is excellent for blast furnaces.

11.[1] Powder brown. Coke *much* puffed out. The small in much request for the making of coke.

12.[2] Powder brown. Coke puffed out.

13.[3] Powder black brown. Coke semi-metallic in lustre, fritted; the particles stick well together. This coal occurs in lower marls of the inferior oolite.

14.[4] Powder brown. This coal is a very brilliant jet; very hard; fracture conchoidal; used for ornamental purposes. Coke semi-metallic in lustre; brilliant; the particles become rounded, and stick together pretty firmly. It occurs in the upper series of the secondary formation (Terrain cretacé).

15—20.[5] In all the coke is described as *well formed*, and in No. 10 it is stated to be well formed and puffed out.

21.[6] Colour pitch black; lustre fatty, here and there passing into vitreous; fracture very uneven; *caking*. From Resicza mine, county of Krassó.

22. Colour of the coal and its powder pitch black; lustre in the direction of the layers fatty, but on the cross fracture glistening. Is very easily pulverized, but does not fall to pieces when exposed to the air. *Strongly caking*. From Fünfkirchen, county of Baranya.

23. Colour pure pitch black; lustre vitreous; compact, difficult to pulverize, yet falls to pieces by exposure to the air, though not to powder. *Strongly caking*. From the same locality as No. 14.

24. Colour of the coal and its powder pure pitch black. Lustre fatty. Easily rubbed to powder between the fingers, and falls to fine powder by exposure to the air. *Strongly caking*. From Szabolcs, county of Baranya.

25. Colour of the coal pitch black. Compact, difficult to pulverize, resists the action of the air, and does not fall to pieces after several years' exposure.

26.[7] From the west coast of the Middle Island. Ash remarkably white. Coke contains 2·35 per cent. of sulphur. No sulphuric acid was detected in the hydrochloric acid in which the powder of the coal had been boiled. It would appear therefore that the sulphur was

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[8] 9. Regnault, Ann. d. Mines, 3. s. 12, p. 189.
[9] 10. Do. do. p. 185.
[1] 11. Do. do. p. 196.
[2] 12. Do. do. p. 200.
[3] 13. Do. do. p. 214.
[4] 14. Regnault, op. cit. 216.
[5] 15—20. M. de Marsilly. Comptes Rendus, 46. 891.
[6] 21—25. By Nendtwich, op. cit. pp. 15-22.
[7] 26. By C. Tookey, in my laboratory.

E8077

British Non-caking Coals.

Number.	Locality.	Specific Gravity.	Carbon.	Hydrogen.	Oxygen.	Nitrogen.	Sulphur.	Ash °/₀.	Water °/₀.	Coke °/₀.	Exclusive of Ash. Carbon.	Hydrogen.	Oxygen.	Nitrogen.
27	South Staffordshire	..	76·12	4·83	16·72	..	1·00	2·33	..	..	78·46	4·96	16·58	..
28	,,	..	77·01	4·71	16·72	..	0·74	1·56	..	..	† 78·53	4·80	16·66	..
29	,,	..	76·40	4·62	17·43 *	..	0·55	1·55	..	..	77·68	4·69	17·62	..
30	,,	..	72·13	4·32	17·11	..	0·54	6·44	..	..	77·32	4·67	17·99	..
31	Nr. Wolverhampton	1·278	78·57	5·29	12·89	1·84	0·39	1·03	11·29	57·21	79·38	5·34	13·02	..
32	St. Helen's, Lancashr.	1·279	75·81	5·22	11·98	1·93	0·90	5·17	3·23	65·50	79·93	5·50	11·58	..
33	Dowlais, S. Wales	..	89·33	4·43	3·25	1·24	0·55	1·20	0·79	..	90·93	4·51	3·30	1·26
34	,,	..	88·13	4·51	2·94	1·41	1·01	2·00	0·68	..	90·86	4·65	3·03	1·46
35	,,	..	87·62	4·34	2·52	1·13	1·07	3·32	0·68	..	91·64	4·54	2·64	1·18
36	,,	..	82·60	4·28	3·44	1·29	1·22	7·18	0·78	..	90·18	4·67	3·76	1·39
37	Scotland	..	76·08	5·31	13·33	2·09	1·23	1·96	..	..	78·59	5·49	13·77	2·15
38	,, ...	..	80·63	5·16	10·61	1·33	0·84	1·43	..	..	82·50	5·28	10·86	1·36
39	,, ...	..	80·93	5·21	10·91	1·57	0·63	6·75	..	..	82·06	5·29	11·06	1·59

* Oxygen found by deducting the sum of the carbon, hydrogen, and ash from 100, exclusive of sulphur.
† Calculated after corrections.—*See text.*

present in the same state of combination in the coal as it exists in albumen, fibrine, &c. It could not have been combined with iron, for in that case the ash would have had a decided red colour. Geologists are of opinion that this coal occurs in strata of miocene age, in which case it presents an example of a coal similar in external characters and chemical constitution to varieties of coal occurring in the true coal measures.

27—30.[8] Thick or ten-yard coal from the vicinity of West Bromwich. This seam consists of ten or more beds, to which special names are applied. No. 27 is "Rooves;" No. 28, "Top-slipper;" No. 29, "White-coal;" and No. 30, "Brasils." No. 30 contains much earthy matter, and is in request for certain reverberatory smelting furnaces in Birmingham. The powder of each of these coals is brownish black. The colour of their respective ashes is as follows:—No. 27, reddish-grey; No. 28, yellowish-red; No. 29, yellowish-red; No. 30, reddish-grey. The portion analysed of each coal was dried somewhat above 100° C. Combustion was effected in oxygen. The total amount of sulphur in each coal was determined, as was also the amount of sulphuric acid in the ashes. No. 27 contained a trace of sulphuric acid.

	Sulphuric acid in the ashes of 100 parts of coal.	Iron in the ashes of 100 parts of coal.	Sulphur required to form iron pyrites with the iron.	Total sulphur in 100 parts of coal.	The + and − signs indicate an excess of sulphur or otherwise.	Pyrites in 100 parts of coal, estimating the whole of the iron as FeS^2, except in No. 4, where the iron is in excess.
No. 27.....	0 24	0·32	0·37	1·00	+0 63	0·69
28.....	0·31	0·12	0·14	0·74	+0·60	0·26
29.....	0 33	0·03	0·034	0·55	+0·52	0·064
30.....	1·31	0·94	1·08	0·54	−0·54	1 01

[8] 27—30. By A. Dick, in my laboratory.

In calculating the composition of these coals in the table, the following corrections have been made:—Deduction from the weight of ash of the oxygen corresponding to the sulphur present as sulphuric acid, the product of oxidation; deduction of the oxygen of the sesquioxide of iron existing in the ash, except in No. 4, in which a deduction of oxygen from the sesquioxide of iron was made equivalent to the proportion of iron required to form bisulphide with the sulphur in the coal, the sulphur in this case being the reverse of excessive; and in No. 30 a correction has been made in the ash by the addition of 2·64 per cent. of carbonic acid $-0·43$ found in the ash ($= 0·72$ of carbon) which was present in the coal as carbonate. Hence the amount of inorganic matter in this coal may be estimated at 7·67, *i.e.* by the addition of the carbonic acid expelled by incineration to the actual amount of ash obtained, and with the correction for the sulphuric acid and sesquioxide of iron as above stated. The 7·67 would consist of iron pyrites 1·01 and 2·64 of carbonic acid in combination in the 4·02 of fixed residual inorganic matter. The first four analyses after these corrections will be:—

	Carbon.	Hydrogen.	Oxygen and Nitrogen.	Sulphur.	Iron Pyrites.	Residue.
No. 27.....	76·12	4·83	16·10	0·63	0·69	1·63
28.....	77·01	4·71	16·35	0·60	0·25	1·08
29.....	76·40	4·62	17·23	0·52	0·064	1·17
30.....	72·13	4·32	16·88	—	1·01	6·66

It is no libel on South Staffordshire to assert that this magnificent bed of coal has been most barbarously treated. The pits have generally been worked by contractors, called butties, under the superintendence of viewers, called ground-bailiffs. In consequence of the rapacity and rascality of many of the former, and the ignorance, inattention, and fraudulent connivance of many of the latter, an enormous amount of coal has been irremediably lost to the nation. Even at the present day the South Staffordshire colliery-viewers are frequently very imperfectly educated for their responsible duties, and the system of colliery mismanagement which still extensively prevails in this part of the country is a disgrace to the age.

31.[9] From the ten yard coal. Coke very lustrous; swells up very much into radiating cauliflower-shaped masses; does not take the form of the crucible. Under ordinary conditions of coking, *i.e.* with the partial admission of air, this coal, which is described as caking, is practically *non-caking*; the small cannot be coked *per se* in ordinary ovens.

32.[1] Rushey Park seam. Slightly caking. Lustre of coke semi-metallic.

33.[2] Upper four-feet coal; seam about 2 feet 9 inches thick; the best

[9] 31. By Vaux, Jo. of Chem. Soc. 1, 328.

[1] 32. By do. do. 321.

[2] 33–36. By E. Riley. Communicated by him to the author.

FOREIGN NON-CAKING COALS.

Number.	Locality.	Specific Gravity.	Carbon.	Hydrogen.	Oxygen.	Nitrogen.	Sulphur.	Ash °/₀.	Water °/₀.	Coke °/₀.	Exclusive of Ash. Carbon.	Hydrogen.	Oxygen.
40	Blanzy, France	1·362	76·48	5·23	16·01	..	..	2·28	..	57·0	78·26	5·35	16·39
41	Commentry	1·319	82·72	5·29	11·75	..	..	0·24	..	63·4	82·92	5·30	11·78
42	Noroy des Vosges.. ..	1·410	64·28	4·35	13·17	..	..	19·20	..	60·3	78·32	5·28	16·30
43	Mons	..	82·91	5·22	10·13	..	..	1·74	..	66·96	84·38	5·31	10·31
44	Ditto	..	82·95	5·42	10·03	..	..	0·70	..	63·58	83·53	5·46	11·01
45	Valenciennes	..	90·54	3·66	2·70	..	..	3·10	..	93·17	93·44	3·78	2·78
46	Pas-de-Calais	..	82·68	4·18	4·54	..	..	8·60	..	87·62	90·46	4·57	4·97
47	Charleroi	..	90·89	3·65	3·98	..	..	1·48	..	91·86	92·26	3·70	4·05
48	Ditto	..	88·69	4·25	5·26	..	..	1·80	..	85·57	90·32	4·32	5·36
49	Hungary	1·423	..	..	..	..	0·58	10·53	3·06	76·33	82·54	4·35	13·10
50	Ditto	1·366	..	..	..	..	0·74	1·55	7·30	70·60	78·37	3·92	17·70
51	Ditto	1·317	..	..	..	..	0·20	1·60	2·66	73·11	85·29	5·05	9·65
52	Ditto	1·319	..	..	..	..	0·87	2·26	3·21	69·98	81·57	4·41	14·01
53	Near Aix-*la*-Chapelle ..	1·313	91·45	4·18	2·12	..	..	2·25	..	89·4	93·56	4·28	2·16

coal at Dowlais. 34. Ras Las: the so-called "brass" (clay iron ore mixed with coaly matter) and iron pyrites are visibly disseminated through this coal. 35. Bargoed big-coal; seam from 7 to 8 feet thick; the cheapest coal. 36. Tomo yard coal; bad coal for blast furnace. All these coals are used in the blast furnaces at Dowlais, and the Ras Las is also used for forges.

37.[3] Ayrshire. 38. Splint coal, Elgin, Fifeshire. 39. Ditto, Five-feet seam.

40.[4] During calcination the particles stick together a little, but separate under the slightest pressure; they keep their form, being only a little rounded on their edges. This coal burns with a good flame, which only lasts a short time. Coke cannot be made with it, but it is esteemed for boilers. It is characterized as a *dry coal with a long flame* (houille sèche à longue flamme).

41.[5] Powder black brown. Coke semi-metallic in lustre, grey, nearly white, very brilliant, and only fritted. Regnault describes this as a true cannel coal.

42.[6] Powder brown. It contains much pyrites disseminated through the whole mass. This coal occurs in the lower series of the Jurassic beds (étage inférieur,—mornes irisées).

43, 44.[7] Coke fritted.

45. Coke not formed.

46. Coke not formed, in powder.

47. Coke not formed, in powder.

48. Coke hardly formed.

49.[8] Colour pitch black; lustre fatty; *non-caking* (Sand-kohle).

50. Grey-black; lustre dull, somewhat fatty; *non-caking* (Sand-kohle).

[3] 37-39. By Rowney. Edinb. New Phil. Journ. 1855. v. 2. p. 141.

[4] 40. By Regnault, Ann. des Mines, 3. s. 12. p. 190.

[5] 41. By Regnault, op. cit. 3. s. 12. p. 193.

[6] 42. By Regnault, op. cit. p. 210.

[7] 43-48. By M. de Marsilly. Comptes Rendus, 1858. v. 46. p. 891.

[8] 49-52. By Nendtwich, op. cit. p. 15.

51. Coal and its powder black; lustre fatty. *Coke fritted* (Sinterkohle).

52. Colour black; but little lustre; difficult to powder, and perfectly resists exposure to the air. *Coke fritted* (Sinter-kohle). All the Nos. from 49 to 52 from the county of Krassó.

53.[9] Powder pure black; it has the vitreous lustre of compact anthracites and the foliated structure of ordinary coals. It is very little changed in appearance by calcination. It occurs at Rolduc. Regnault regards it as a link between anthracites and bituminous coals.

CANNEL COALS.

Number.	Locality.	Specific Gravity.	Carbon.	Hydrogen.	Oxygen.	Nitrogen.	Sulphur.	Ash °/₀.	Water °/₀.	Coke °/₀.	Exclusive of Ash. Carbon.	Hydrogen.	Oxygen.	Nitrogen.
54	Wigan	1·317	81·07	5·71	7·82	..	..	2·40	..	59·0	85·81	5·85	8·34	..
55	Ditto	1·276	80·07	5·53	8·10	2·12	1·50	2·70	0·91	..	82·29	5·68	8·31	..
56	Tyneside	1·319	78·06	5·80	3·12	1·85	2·22	8·94	..	..	87·86	6·53	2·53	2·09

54.[1] Colour black brown, without lustre; powder black brown. Coke silvery metallic grey, very brilliant, only fritted. The particles keep their form, but stick together.

55.[2] Coke hard, semi-metallic lustre, swells up and takes the form of the crucible.

56.[3] Black, homogeneous, hard, brittle. Fracture conchoidal. Susceptible of a fine polish. From "Blaydon Main" Colliery, Tyneside. It is often found in connection with the coal (Buddle's Hartley), as roof, base, or even interstratified with it.

BRITISH AND FOREIGN ANTHRACITES.

Number.	Locality.	Specific Gravity.	Carbon.	Hydrogen.	Oxygen.	Nitrogen.	Sulphur.	Ash °/₀.	Water °/₀.	Exclusive of Ash. Carbon.	Hydrogen.	Oxygen.
57	South Wales, near Swansea	1·348	92·56	3·33	2·53	..	..	1·58	..	94·05	3·38	2·57
58	South Wales	1·392	90·39	3·28	2·97	0·83	0·91	1·61	2·00	91·87	3·34	3·02
59	Pennsylvania	1·462	90·45	2·43	2·45	..	..	4·67	..	94·89	2·55	2·56
60	Ditto	..	92·59	2·63	1·61	0·92	..	2·25	..	94·72	2·69	2·58*
61	Ditto	..	84·98	2·45	1·15	1·22	..	10·20	..	94·64	2·73	2·64

* Inclusive of Nitrogen.

57.[4] Anthracite used at the Yniscedwin blast furnaces. Powder pure black.

58.[5] Bright metallic lustre. Does not soil the fingers. Burns without smoke.

[9] 53. By Regnault, Ann. des Mines, p. 184.
[1] 54. By Regnault, op. cit. p. 191.
[2] 55. By Vaux, Jo. of Chem. Soc. 1. 320.
[3] 56. By Taylor, Edinb. New Philos. Journ. 1851. v. 50. p. 145.
[4] 57. By Regnault, op. cit. 183.
[5] 58. By Vaux, op. cit. 324.

59.[6] From Pittsville. Powder pure black. The sides of the fissures are beautifully iridescent.

60.[7] Lustre shining. From the Lehigh Summit Mine, Pennsylvania, U.S. I received this specimen from Sir C. Lyell.

61.[8] Lustre somewhat glistening; powder black. From Mauch-Chunk, the shipping place of the Lehigh coal, at the eastern end of the southern anthracite basin.

In the following table is presented, for the sake of illustration, a selection of analyses of the ashes of various coals :—

COMPOSITION OF THE ASHES OF COALS.

	1.	2.	3.	4.	5.	6.	7.	8.	9.
Silica	35·73	24·18	37·61	39·64	40·00	53·00	37·60	43·68	53·60
Alumina	41·11	20·82	38·48	39·20	44·78	35·01	52·00	39·34	36·69
Sesquioxide of iron	11·15	26·00	14·78	11·84				8·22	5·59
Lime	2·75	9·38	2·53	1·81	12·00	3·94	3·73	5·76	2·86
Magnesia	2·65	9·74	2·71	2·58	Trace.	2·20	1·10	3·00	1·08
Oxide of manganese	..	..	..	..	..	..	..	..	0·19
Sulphuric acid	4·45	8·37	0·29	Traces.	2·22	4·89	4·14	..	..
Phosphoric acid	0·99	0·21	2·00	3·01	0·75	0·88	0·88	..	..
Sulphide of iron (FeS)	..	0·38	..	..	..	..	..	..	..
	98·83	99·08	98·40	98·08	99·75	99·92	99·45	100·00	100·01

Nos. 1–4[9] are analyses of the ashes of the Dowlais coals, numbered from 33 to 36 respectively. No. 5. Rock Vein coal, Pontypool. No. 6. Four-feet steam-coals, Ebbw Vale. No. 7. Fordel splint coal, Fifeshire, Scotland. Nos. 8, 9. Anthracites of the United States.

On the occurrence of certain metals in coals.—Daubrée has detected traces of arsenic and antimony in the coal of Newcastle-on-Tyne; in the coal of Sarrebrück he found 0·003 per cent. of arsenic; and in a variety of coal occurring at Villé (Bas-Rhin), in France, as much as 0·0415 per cent., besides traces of antimony and copper.[1] The same observer, as previously stated, detected arsenic in certain lignites. The Nottinghamshire coal (No. 5, Table p. 99) contained decided traces of arsenic. I have seen galena in coal from Bedworth, Warwickshire. The anthracite of South Wales, which we have been accustomed constantly to employ in the metallurgical laboratory of the School of Mines, contains decided traces of copper.

Frémy's chemical researches on combustible minerals.[2]—These researches have been published since the preceding article on coal was in type. The following is a résumé of the chief results:—1. *Lignite.* The varieties known as *bituminous wood* are, like peat, partially soluble in alkalies, but they dissolve almost completely in nitric acid and the

[6] 59. By Regnault, Ann. des Mines, 180.

[7] 60. By the Author. Proceedings of the Geolog. Soc. 1. 202.

[8] 61. By the Author, op. cit.

[9] Nos. 1—4. By E. Riley. Communicated to the Author. Nos. 5—7. First Report on the Coals suited to the Steam Navy, by Sir Henry De la Beche and Dr. Lyon Playfair. Museum of Practical Geology, London, 1848. Nos. 8, 9. By Walter R. Johnson: A Report to the Navy Department of the United States on American Coals applicable to Steam Navigation and to other purposes. Washington, 1844.

[1] Recherches sur la présence de l'arsenic et de l'antimoine dans les combustibles minéraux, etc., par M. A. Daubrée, ingenieur des mines, Ann. d. Mines, 4 s. 19, p. 669. 1851.

[2] Comptes Rend. 52, p. 114. Jan. 1861.

hypochlorites. The *compact* and *black varieties* resembling bituminous coal are in general not acted upon by alkalies, but dissolve completely in hypochlorites and in nitric acid. 2. *Bituminous coals.* They do not dissolve either in alkaline solutions or in hypochlorites. Both bituminous coals and anthracite dissolve completely in a mixture of monohydrated sulphuric acid and nitric acid; a dark brown solution is produced, containing an *ulmic* compound, which is entirely precipitated on the addition of water.

CHARCOAL.

When wood is heated without access of air to about 300° C[3]., it is resolved into volatile products, and a fixed residue or charcoal. The volatile products consist of water, acetic acid, tar, and other matters which are condensable, and of the permanent gases, carbonic acid, carbonic oxide, hydrogen, and carburetted hydrogen. This process of decomposition of organic compounds by heat without access of air is known as that of *dry distillation* or *carbonization*. Charcoal is extremely porous, and retains the structure of the wood from which it is derived. It consists essentially of carbon and of the fixed or inorganic matter which exists in wood; but if carbonization be imperfectly effected, it may contain a sensible amount of hydrogen. Wood may in a great degree be carbonized at 220° C., but not completely below a red heat.[4] Good charcoal is black, gives a sonorous ring when struck, breaks with a more or less conchoidal fracture, does not crumble under moderate pressure, although it is brittle under a blow, does not sensibly mark the finger when it is rubbed against a freshly fractured surface, or make a mark which cannot easily be rubbed off, swims on water, and does not burn with flame when ignited in separate pieces. It is a bad conductor of heat and electricity; but its conducting power is increased after it has been exposed to a high temperature. One end of a short piece of common charcoal may be held in the hand without inconvenience while the other end is burning actively; but this could not be done with impunity with a short piece of charcoal which has been strongly heated.

Violette states that charcoal made at 260° C. burns most easily; but that made between 1000° and 1500° C. cannot even be ignited like ordinary charcoal. Charcoal made at a constant temperature of 300° C. takes fire in air when heated between 360° and 380° C., according to the nature of the wood from which it has been derived; charcoal from light woods, *cæt. paribus*, burning most easily. Charcoal made between 260° C. and 280° C. ignites between 340° and 360° C.; that made between 290° C. and 350° C. between 360° and 370° C.; that made at 432° C. burns at about 400° C.; that made between 1000° and 1500° C.

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[3] Jahresbericht über die Forts. der Chem. Technologie, Wagner, 1857, p. 474.

[4] I have obtained the following results concerning the temperature at which carbonization may be effected. A narrow test-tube, containing a thin strip of deal, was depressed in mercury to the depth of an inch or two with the closed end downwards, and the temperature of the mercury was gradually raised. At 220° C. the wood became perceptibly brown, at 240° it became sensibly darker, and at 255° very brown. It was kept for some time at 280°, when it became deep brown-black. At 310° it became very brittle, and could easily be pulverized.

between 600° C. and 800° C.; and that made at the melting-point of platinum only inflames at about 1250° C. Violette, it will be perceived, applies the term charcoal to very imperfectly carbonized, scarcely more than desiccated, wood.[5]

Owing to its highly porous structure, charcoal has the power of absorbing and condensing gases in considerable quantity. The following Table indicates the amount in volume of various gases which a given volume of freshly burnt charcoal is capable of absorbing.

Ammonia	90	Carbonic oxide	9·42
Hydrochloric acid gas	85	Oxygen	9·25
Sulphurous acid	65	Nitrogen	7·5
Sulphuretted hydrogen	55	Hydrogen	1·75
Carbonic acid	35		

From these data it would appear that the volume of gas absorbed is great in proportion to the condensability of the gas by pressure. It readily absorbs from 10 to 12 per cent. of its weight of aqueous vapour, and may even absorb as much as 20 per cent. Charcoal made at a low temperature absorbs moisture more rapidly and in a greater degree than that made at a high temperature. The power of charcoal to absorb moisture is much affected by the temperature at which it was produced; the lower the temperature the greater the power. Thus charcoal prepared at 150, 250, 350, 430, and 1500 degrees Centigrade, absorbs 21, 7, 6, 4, and 2 per cent. respectively of moisture by exposure to a moist atmosphere. Charcoal in powder absorbs about twice as much moisture as the same charcoal in pieces.[6] The proportion of water which it retains will necessarily vary with the state of the atmosphere in respect to moisture. Commercial charcoal may be estimated to contain not less than 9, generally about 12, per cent. of moisture (Karsten, Scheerer); and when heated to whiteness, it loses from 14 to 15 per cent. of combustible gases and aqueous vapour (Berthier).

The specific heat of ordinary charcoal, according to Regnault, is 0·2411. The specific gravity of charcoal varies with the nature of the wood from which it is made, with the age of the wood, with the state of the wood as to dryness, and with the process of carbonization. New and accurate determinations of the specific gravity of charcoal from different kinds of wood, with statements as to the age of the wood, mode of carbonization, &c., are needed. In the old Table of Hassenfratz, the specific gravity of charcoal, *inclusive* of the pores, ranges from 0·203 in birchwood charcoal, to 0·106 in limewood charcoal, that of oak being 0·155 or intermediate. The specific gravity of charcoal according to Violette, *exclusive* of pores, that is after perfect replacement of the air contained in the pores by water, ranges from 1·402 to 2·002, according as it has been prepared at temperatures between 150° C. and 1500° C. respectively.[7] A knowledge of the specific gravity of charcoal is of no practical value, because the amount of matter absorbed may vary considerably according to circum-

[5] Ann. de Ch. et de Phys., 3, s. 39. 1853. [6] Violette, op. cit. [7] Do., 340.

stances; and because, owing to difference of size and form in the pieces of charcoal, there may be likewise great variation in the amount of interstitial space (Karsten). It has been accurately determined at the Prussian iron-works, that 1 cubic foot of charcoal of Scotch fir weighs from 10·3 to 10·9 pounds avoirdupois; and that 1 cubic foot of oak or beech charcoal weighs from 13·2 to 14·1 pounds.[8]

The proportion of ash in charcoal will obviously vary with the nature of the wood. On the average it may be estimated at about 3 per cent.[9] But on reference to the Table of the composition of various kinds of wood, it will be seen that the proportion of 3 per cent. of ash may be greatly exceeded. Knowing the percentage of ash in any given wood, and estimating the average yield of charcoal at 23 per cent.[1] by weight, the proportion of ash in the charcoal may be calculated.

Commercial charcoal, even when well burnt, contains a sensible amount of hydrogen and oxygen, as Bunsen and Playfair have demonstrated.[2] They analysed the gases evolved from various specimens of charcoal heated in close vessels. Their results are as follows:—

	1.	2.	3.	4.
Carbonic acid	23·65	15·96	19·58	35·36
Carbonic oxide	15·96	13·62	20·57	14·41
Hydrogen	43·39	50·10	39·10	29·45
Carburetted hydrogen	11·00	20·32	20·75	14·41

1. Very well burnt charcoal from beechwood.

2. Well burnt firwood charcoal.

3. Well burnt oak charcoal—0·65 gramme, gave of carbon 0·47, and 70 cubic centimetres of gas, at 0° C. and 0·76 bar.

4. Imperfectly burnt beechwood charcoal, pulverulent and of a blackish-brown colour,—0·733, gave of carbon 0·443, and 250 cubic centimetres of gas, at 0° C. and 0·76 bar.

Ebelmen has determined the composition of the charcoal of poplar and young oak, obtained by charring in piles.[3] Both were dried between 140° and 150° C. The oak charcoal had been long exposed to the air. The poplar charcoal lost 5·2 per cent., and the oak charcoal 6 per cent. in weight by desiccation at the temperature above stated. The loss by exposure to a white heat in a platinum crucible was also ascertained. The results are given in the following Table.

	Poplar.		Oak.		Loss by exposure to a white heat.	
					Poplar.	Oak.
		Ash deducted.		Ash deducted.		
Carbon	87·22	87·98	87·68	90·46	17·07 per cent.	13·06 per cent.
Hydrogen	3·20	3·22	2 83	2·91		
Oxygen	8·72	8·80	6·43	6·63		
Ashes	0·86	..	3·06	..		

[8] Handwörterb. der Chemie, 4, 443.

[9] Richard, Etudes sur l'Art d'extraire immédiatement le Fer de ses Minérais, p. 48.

[1] Scheerer, Handb. d. Met. p. 254.

[2] British Assoc. Rep. 1846, p. 145.

[3] Recueil des Trav. Scient. 2. 228.

Faisst has found the composition of several kinds of charcoal to be as follows:—

	1.	2.	3.
Water	7·23	6·04	8·21
Carbon	88·89	85·18	87·43
Hydrogen	2·41	2·88	2·26
Oxygen with nitrogen	1·46	3·44	0·54
Ash	3·02	2·46	1·56

1. Beechwood charcoal from piles. 2. Hard charcoal from wood vinegar works. 3. Light charcoal from wood-gas works.[4]

The proportion of hydrogen and oxygen existing in *dry* charcoal will depend upon the temperature at which carbonization has been effected: the higher the temperature the greater will be the amount of carbon in charcoal. Violette has analysed charcoal prepared from the same wood at gradually increasing temperatures, from that at which carbonization commences to that at which platinum melts. His most important results are contained in the following Table.[5]

No.	Temperature in Centigrade degrees at which carbonization was effected.	Composition of charcoal produced. Carbon.	Hydrogen.	Oxygen, Nitrogen, and loss.	Ashes.	Observations.
1	150	47·51	6·12	46·29	0·08	The products obtained at these temperatures cannot properly be termed charcoal, but merely desiccated wood.
2	200	51·82	3·99	43·98	0·23	
3	270	70·45	4·64	24·19	0·85	
4	350	76·64	4·14	18·44	0·61	
5	432	81·64	1·96	15·24	1·16	melting-point of antimony.
6	1023	81·97	2·30	14·15	1·60	do. silver.
7	1100	83·29	1·70	13·79	1·22	do. copper.
8	1250	88·14	1·41	9·26	1·20	do. gold.
9	1300	90·81	1·58	6·49	1·15	do. steel.
10	1500	94·57	0·74	3·84	0·66	do. iron.
11	Beyond 1500	96·52	0·62	0·94	1·94	do. platinum.

No. 3 was what the French term "très roux," from its yellowish-red or rusty colour; it was beginning to be pulverisable. No. 4 was black charcoal like that of all the succeeding numbers. The results of Nos. 6 and 7 are somewhat discordant; but it must be difficult, if not impracticable, to insure perfectly harmonious results in experiments of this kind. The wood operated on was that of Rhamnus Frangula, which furnishes a charcoal suitable for gunpowder: it was dried at 150° C.

The following Table will serve as a companion to the last, and is interesting as showing the amount of carbon and other matter expelled during carbonization at different temperatures.[6]

[4] Wagner, Jahresber. 1856, p. 457.
[5] Ann. de Ch. et de Phys. 3. s. 32, 322. 1851.
[6] Violette, op. cit. p. 325.

Temperature in Centigrade degrees at which carbonization was effected.	Products of the decomposition of Wood by carbonization.					General Total of Products.
	Solid matter or charcoal in 100 parts.			Matter volatilised and carried over in 100 parts.		
	Carbon.	Gaseous elements.	Ashes.	Carbon.	Gaseous elements.	
150	47·51	52·41	0·08	—	—	100
200	39·95	36·97	0·18	7·56	15·34	do.
270	26·17	10·65	0·32	21·34	41·52	do.
350	22·73	6·75	0·18	24·78	45 56	do.
432	15·40	3·25	0·22	32·11	49·02	do.
1023	15·37	3·12	0·30	32·14	49·11	do.
1100	15·32	2·86	0·22	32·19	49·41	do.
1250	15·81	1·91	0·22	31·70	50·36	do.
1300	15·86	1·40	0·20	31·65	50·89	do.
1500	16·37	0·83	0·11	31·14	51·55	do.
Beyond 1500	14·48	0·23	0·29	33·03	51·97	do.

VARIOUS MODES OF CHARCOAL-BURNING.—Charcoal-burning is effected in the open air in piles or stacks provided with a yielding cover, in pits, in closed chambers of brick or stone, and in iron retorts heated externally like common gas-retorts. I shall not present any description of the latter method, which is practised by the manufacturers of pyroligneous acid and gunpowder, and is not specially within the province of the metallurgist.

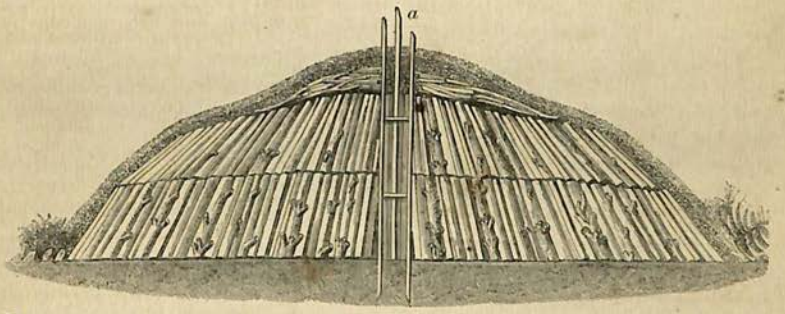

Fig. 2.
Vertical section through the centre of a pile, from Karsten's Atlas, No. 301. At the foot on the left the cover is shown resting on stones, and on the right it is shown resting on branches supported by forked sticks.

Charcoal-burning in piles or stacks.—Dry level ground, well sheltered from the wind, and near a water-supply, should be chosen as the site. When the pile is circular, the bed on which it rests should have a slight inclination upwards, from the circumference to the centre. In the centre three upright stakes are driven in about a foot equi-distant from each other, *a*, fig. 2, and so secured that they may resist pressure from without. This may readily be done by means of pieces of wood placed crosswise from stake to stake, or by suspending a block of wood within the stakes. Pieces of wood of equal length are piled concentrically around the stakes, placing those nearest the centre almost

vertical, and giving the surrounding pieces a slight but gradually increasing inclination. A second row, and in the case of very large piles even a third, may be stacked in a similar manner, one above another. The wood should be packed as close as possible; and all large interstices due to irregularity of shape in the pieces should be filled with the small wood of branches. The top of the pile is covered with a layer of the same kind of small wood, placed horizontally and radially, so that the whole pile may have the form of a truncated cone, rounded at its upper and smaller end. Close to and round the base of the pile a row of forked sticks is driven in, with the forked ends uppermost and about six inches out of the ground. The pile is then encircled with a band of branches, resting in the forks of these sticks. This band supports the cover of the pile which has next to be applied. A row of stones or pieces of wood may be used for the same purpose. The surface of the pile is made more or less even by packing in here and there bits of wood or small branches. The whole pile above the band of branches is now covered, except the space at the top of the three central stakes, with turf, placing the *grassy side inwards;* and if turf cannot be got, leaves or moss may be used. The turf is plastered over with a layer some inches thick of the soil which may be at hand, or, when procurable, with a mixture of the residual charcoal-dust of previous burnings and soil, moistened sufficiently with water. As a rule the cover should be most solid and thickest at the top of the pile, where it is longest and most exposed to the action of heat. The pile is now ready for lighting. It is desirable that this should be done early in the morning, and during fine weather, because at first much attention is required on the part of the charcoal burner; and because it is important that the pile should be well and regularly kindled, a condition which cannot be ensured in bad weather. The space within the three central stakes or chimney is filled with easily inflammable wood, which is then ignited, and the fire is kept up by a supply of fresh wood or charcoal, until the centre of the pile has become thoroughly kindled. Any sinkings-in which may occur at the top of the pile must be made good by taking off the cover from that part and putting in fresh wood. The chimney is afterwards well filled with small dry wood or charcoal, and effectually stopped by extending the turf and soil covering over it and pressing it well down. In this, the *first* or *sweating* stage of the process, much water condenses in the cover, and especially appears round the base or foot of the pile, which is left uncovered below the band of branches; during this stage, without proper attention on the part of the charcoal burner, explosions are apt to occur, occasioned by the ignition of explosive mixtures of atmospheric air and the inflammable gaseous products of the carbonization. That the explosions are due to this cause would appear from the fact that they are stated never to occur when much steam escapes from the cover, and that they very frequently occur when dry and resinous wood is used.[7] Karsten, however, attributes

[7] Wehrle, Lehrbuch, 1. 309.

these explosions to the sudden escape of steam. When the sweating stage is over, the foot of the pile is covered, and any hollows which may be found by probing with a pole are filled up. The cover in every part is made solid and impervious to air, and the pile is left to itself during three or four days, the heat existing in it being sufficient to effect the carbonization of much of the surrounding wood. If left too long in this state the fire would be extinguished, to prevent which holes or vents are made in the cover round the pile, on a level with the top of the first row of wood (fig. 2). Thick yellowish-grey smoke at first escapes from these vents, but after a time it becomes bluish and nearly transparent. The vents are then stopped, and another row below them is opened, when the same change in the appearance of the smoke ensues. The character of the smoke indicates exactly the degree of carbonization in that part of the pile from which it issues. If necessary, after the stopping of the second row of vents, a third may be opened about nine inches or so below. These vents serve for the *escape* of the volatile products of the carbonization, and not for the admission of air, which enters chiefly at openings made at the foot of the pile. When only bluish transparent smoke proceeds from the lowest vents, every part of the surface must be well covered and rendered as impervious to the admission of air as practicable. The position of the vents may be varied according to circumstances. The object of the charcoal burner should be to conduct the combustion as uniformly as possible from the top towards the bottom, and from the centre towards the circumference of the pile. By making a vent in any part of the pile, he has the power of establishing a current of air through, and, consequently, of increasing the combustion in, that part. During the process of carbonization wood decreases considerably in volume, so that the degree of regularity in the contraction of a pile during the progress of burning is a measure of the regularity with which the process has been conducted. The cover being yielding, adapts itself to the gradually decreasing size of the pile. The pile is left at rest during a few days, after which the charcoal may be drawn, beginning on one side, at the bottom, and from this point proceeding all round, care being taken to cover up the pile as the charcoal is drawn, and to quench the latter with water. If water cannot be had, the charcoal must be covered with the dust of previous burnings, or with dry soil. If the pile were left to itself, it would in time be perfectly extinguished; but experience has shown that the charcoal in that case is less serviceable than that which is rapidly extinguished.[8]

The method of charcoal-burning just described is extensively practised; and in respect to *yield* and *quality* of charcoal, it is not, when properly conducted, surpassed by any other. It has the advantage of not requiring any permanent construction, so that the timber may be burned on the spot on which it is felled, and thus the expense of carriage to a distance may be greatly diminished, as the

[8] Karsten, Sys. d. Metall. 3. 69.

wood weighs about five times as much as the charcoal produced. It may be modified in details according to local circumstances, and the practice of the charcoal burner.

a c, fig. 3, represents a vertical section of half a pile, similar to that shown in fig. 2, but with a different method of supporting the cover,

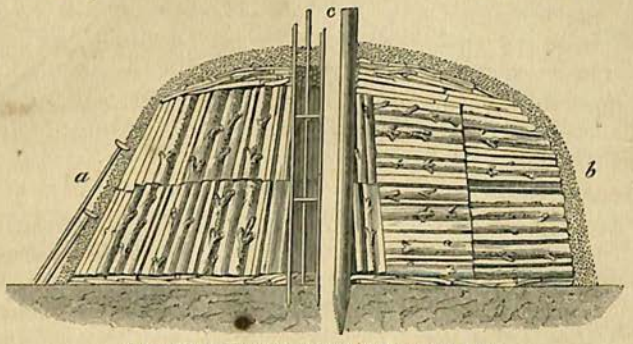

Fig. 3. Copied from Nos. 302 and 300 of Karsten's Atlas.

namely, by boards placed horizontally round the pile, resting on wooden props, *a*. *c b* is a vertical section of the half of another kind of pile described farther on.

1. The three central stakes may be replaced by one, *c*, fig. 3; but in this case it is necessary to construct a channel from the outside of the base of the pile, by means of which burning fuel may be introduced so as to ignite the wood at the bottom of the central stake, immediately around which easily combustible matter should be placed. For this purpose imperfectly charred wood from a previous burning may be used. When the pile is well kindled, the channel must be stopped. The channel may be made, either by leaving a space between the billets at the bottom, or by making a furrow in the bed of the pile. Pieces of wood may be placed upon the bed, radiating from the centre as in fig. 4, and the channel formed by two parallel pieces as at *a*; pieces of wood are next arranged concentrically, as shown in one-half of the figure, and so a firm foundation of wood is made for the pile. The outer dark ring in the cut is the dust of charcoal or *breeze*[9] covering the bed of the pile. Fig. 5 is a vertical section of a pile through the centre. Around the central stake *b* is packed easily inflammable

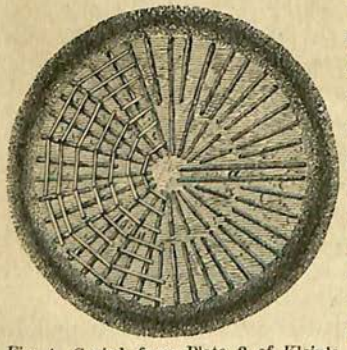

Fig. 4. Copied from Plate 2 of Klein's Treatise.

[9] I use this word *breeze* to denote the small residual charcoal obtained in charcoal-burning, just as the coke-burner applies it to the small residual coke obtained in coke-burning. It is derived from the French word *braise*, which is applied to the residual charcoal obtained in the heating of bakers' ovens. It is drawn out, extinguished with water, and sold under the name of braise.

wood, such as the imperfectly carbonized pieces termed *brands* from a previous burning. The lower part of the cover is supported by stakes *c*: in the middle of each of these stakes is fixed, at right angles, a piece of wood *d*. Resting upon the tops of the stakes *c* are boards *e*, extending round the pile. These boards support the cover from *e* to *f*. The upper part of the pile is propped all round by poles, on the top of each of which is fixed a cross-piece, as shown at *f*, fig. 5, and in fig. 6, in which one is seen lying in the foreground to the left. The pile is left uncovered round the zone *g*, for some time after ignition. The cut fig. 6 represents a pile of this kind, of which the height is 16 feet: the man

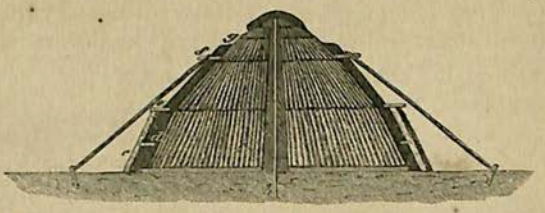

Fig. 5. Copied from Plate 2 of Klein's Treatise.

Fig. 6.

on the plank is engaged in carrying up the breeze with which to complete the cover at the top; in the left foreground are various implements used by the charcoal burner; the scene is Ruhpolding in Bavaria, and the artist is Mr. Justyne, who, with the exception of the picturesque group of figures, has derived the materials of his drawing from the plates in the work of Klein.[1] The channel may be omitted,

[1] Ueber Verkohlung des Holzes in stehenden Meilern. Von Ferdinand Klein. Gotha, 1836.

and a central stake fixed, extending upwards about one-third of the highest part of the pile, a hollow space being left above the stake for the purpose of igniting in the manner first described.

2. The wood may be piled horizontally and radially in concentric rows, *b*, fig. 3. The spaces between the pieces will be wider towards the outside than towards the centre, and these must be well packed with small wood. By sawing the wood to suitable lengths, the pieces may be so piled as to form a series of steps round the outside of the pile, which will tend to prevent the cover from slipping off. By this means of supporting the cover, the pile may be made much steeper, a condition favourable to complete carbonization of the whole mass. The outer ends of the pieces upon which the cover rests are less cooled in steep piles than in flat ones.[2]

3. The pieces may be piled at first vertically round the axis for some distance, and then horizontally as in fig. 3, *b*. In this arrangement Karsten remarks that the hollow spaces are reduced to a minimum; and with pieces of equal length the outer ends of the last row naturally form a series of steps by which the cover may be firmly supported. It is especially necessary, in a pile of this kind, to cover the bed with a layer of waste pieces of wood, in order that the charring may extend well to the bottom (Karsten). There has been much discussion whether it is most advantageous to stack the wood vertically or horizontally, and practical charcoal-burners are still far from unanimous on the subject. Experimental results have been advanced in favour of each method of stacking.

4. A conical cavity, lined with brick, 1^m 33 (4 ft. 4¼ in.) in diameter at the top, 0^m 50 (1 ft. 7¾ in.) at the bottom, and 0^m 50 (1 ft. 7¾ in.) deep, is made in the centre of the bed. Three brick flues, 0^m 12 (4¾ in.) on the side, proceed from the bottom of this cavity, and communicate with the external air beyond the base of the pile. The cavity is filled with small wood and imperfectly charred pieces, and then covered with sheet iron. The construction is similar to that described by Karsten, and which is represented in woodcut No. 7. The diameter of the pile at the base is 9 metres (29 ft. 6¼ in.); the wood is sawn in lengths of 0^m 67 (2 ft. 2½ in.), and piled vertically in three rows one above another. In every part corresponding to the projection of the cavity beneath, a thick layer of soil and small charcoal is put upon the first row of wood, but in other respects the pile is made in the usual way; care being taken to diminish the interstices as much as possible, and to stack each piece in a diametral plane passing through the axis of the pile. The fuel in the cavity is then ignited. The upper part of the pile is uncovered, and holes are opened round the base. When it is well kindled, the three flues above-mentioned are closed, the top is covered, and the process conducted as usual. From 28 to 35 cubic metres (989 to 1236 cub. ft.) of wood may thus be burned in four or five days. At Audincourt, where this process is practised,

[2] Karsten, Sys. d. Metall. 3. 55.

it has been found better to operate upon this quantity of wood than upon 150 or 180 cubic metres (5298 to 6357 cub. ft.) at a time, as was formerly done.[3] The advantage of this method is, that it obviates the necessity of repeatedly charging the centre of the pile with fresh wood during some time after lighting; but it is not adapted to charcoal-burning in forests, where the site of the pile is constantly changed; nor can it well be employed in very moist soils, on account of the difficulty of kindling the wood in the cavity. Moreover, another advantage in these small piles is, that the charcoal burner can more easily manage them than large ones.

5. When carbonization can be economically conducted in one spot, a permanent bed of brickwork may be constructed, with an arrangement

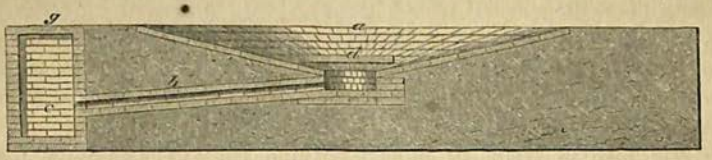

Fig. 7. Copied from No. 297 of Karsten's Atlas.

for collecting tar and pyroligneous acid. Fig. 7 [4] represents a vertical section through the centre of such a bed *a*. It slopes *towards* the centre, and not *from* it as in the ordinary pile. At the bottom in the centre, there is a cylindrical cavity, from which proceeds a channel *b* to a reservoir *c*, provided with a moveable cover *g*, such as a plate of iron; *d* is a square plate of iron, of which the corners are rounded. The tar and other liquid products condense and trickle down between the sides of the plate *d* and the brickwork, and flow into the reservoir *c*. The pile is stacked up in the usual way. Care must be taken to prevent access of air through the channel *b*.

6. Charcoal-burning in large rectangular piles is extensively practised in some parts of Sweden. Af Uhr has published a detailed account of the process, of which I avail myself in the following description.[5] The ground on which the pile rests should be solid, dry, and even, free from roots and stones, and should slope gradually from one end to the other, about 18 inches in 24 feet. The base is *usually a square of 20 feet on the side* or upwards. Upon the ground, *in the direction of the slope*, three poles, *a a a*, fig. 8, are placed parallel to each other, one in the middle and the other two about 2 feet from the sides of the pile respectively. These poles may be 6 or 7 inches in diameter at one end, and 4 or 5 at the other; the thickest ends should be placed at the upper part of the slope. At the lower end or *foot* of the pile are firmly fixed two posts, *b b*, inclining somewhat towards the pile, and supported by props on the outside, *b'*, fig. 9.

[3] Ebelmen, Trav. Scient. 2. 106.

[4] Karsten's Atlas, No. 297, Sys. d. Met. 3. p. 51.

[5] Anleitung zur vortheilhaften Verkohlung, p. 35. See also Notes by Durocher, Ann. des Mines, 5 ser. 9, p. 359. 1856. I have also received a MS. description from my friend Andreas Grill, of Sweden.

At this end and all along the bottom, the longest and thinnest pieces of wood are placed crosswise on the three poles forming the foundation. The largest pieces should be placed in the centre, and towards the high end or *back* of the pile, where the heat will be greatest. The large and small ends of the pieces should be placed alternately, so that

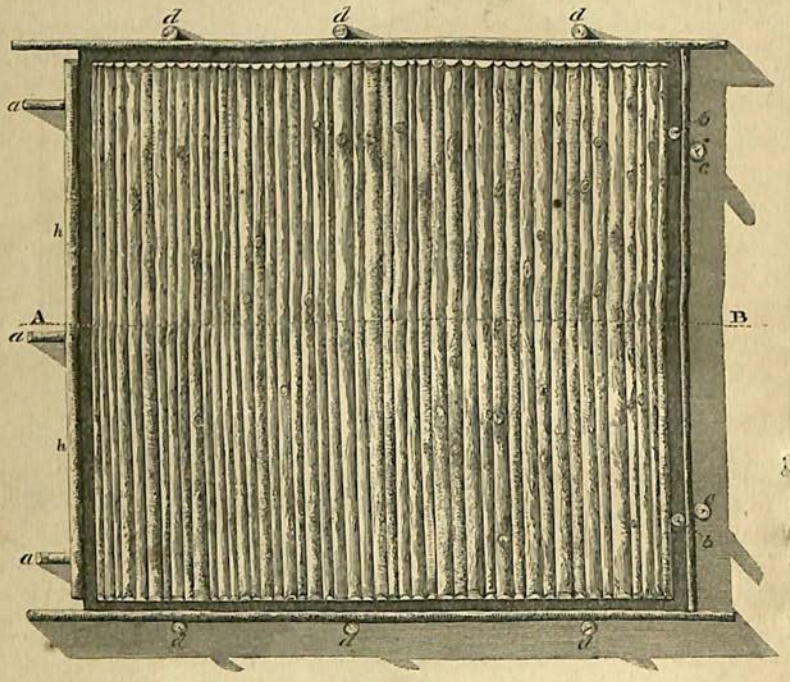

Fig. 8. Plan of the Pile.
Copied from Plate 3 of Af Uhr's Treatise. The inclined props on each side have been omitted.

the pile may be level and compact; the sides formed by the ends of the pieces of wood should be even and vertical. It is not necessary to split the wood, for Af Uhr found that pieces 23 feet long, 2 feet in diameter at one end, and rather more than 1½ at the other, were as thoroughly carbonized in piles of this description as the smaller pieces near them. It is hardly necessary to remark that wood of these dimensions is not used for charcoal-burning when it can be more profitably disposed of as timber. A hole, *k*, fig. 9, 6 inches square, should be left *through* the pile from side to side, near the foot, at about 9 inches from the top. At the back the lowermost piece of wood, *f*, should be let *into* the three poles underneath. Upon this piece at about 3 feet from each end is placed, at right angles, a wedge-shaped piece of wood, *g*, about 3 feet long and 5 inches thick at the thick end, which is directed outwards. Upon the wedges a second piece of wood, *f'*, is placed transversely, and so alternately wedges and wood until the pile is completed, as shown in fig. 9, which is a vertical section on the line A B, fig. 8. By means of these wedges the transverse pieces of wood, *f*, *f'*, &c.,

are supported, and from the bottom to the top of the pile, at this end, is formed a series of parallel openings, which extend inwards as far as the thin ends of the wedges, and which are intended as *draught openings*. The upper surface of the pile is made level by covering it with

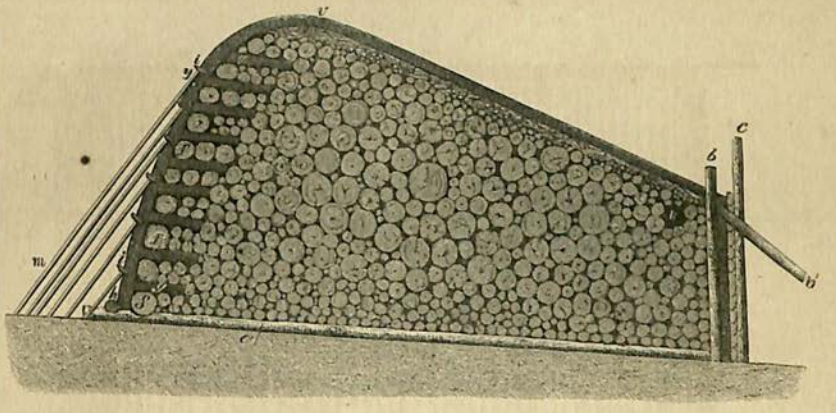

Fig. 9. Vertical Section along the line A B, fig. 8. Copied from Plate 4 of Af Uhr's Treatise.

a layer, 4 inches thick, of small pieces of wood. The larger openings in the sides of the pile must be packed with suitable pieces of wood, and the smaller ones with brushwood. The upper surface of the pile is next covered with fir branches or twigs of sufficient thickness to feel soft under foot. Over the *foot* and the upper transverse pieces of wood at the *back* the brushwood is bent down, and the depending

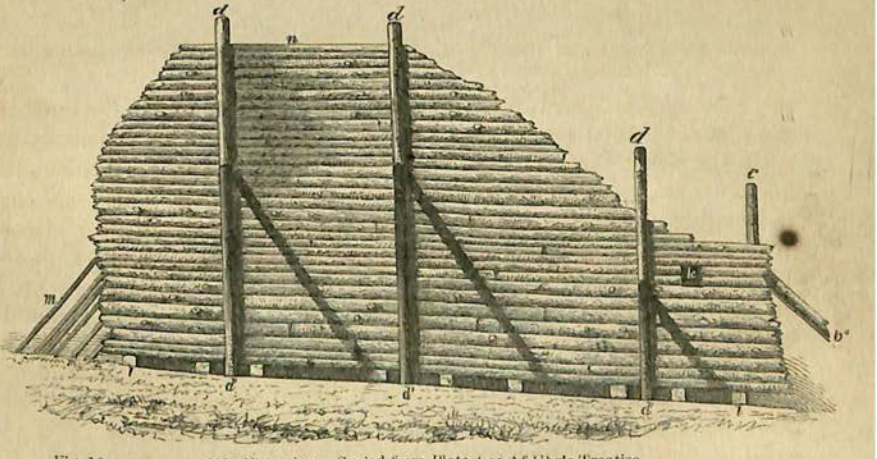

Fig. 10. Side Elevation. Copied from Plate 4 of Af Uhr's Treatise.

ends inserted in the interstices of the pile. The sides of the pile are also covered thinly with brushwood, by sticking the thick ends into the spaces between the pieces of wood, so that the other ends hang

down. The pile is thus prepared to receive its outer carbonaceous or *black-coating* of *breeze* from previous burnings, mixed in a greater or less degree with soil, and moistened with water to the consistency of thick paste. Two posts, *c c*, fig. 8, are firmly fixed in the ground in front, and three, *d d d*, on each side, supported by props. Chips and twigs are carefully swept away round the bottom of the pile; for if they were left, they might cause irregularity in the admission of air into the pile. The black-coating is first applied along the top, over the brushwood, to the depth of 6 or 8 inches. At the back of the pile a piece of wood, *h*, fig. 8, is fixed across the projecting ends of the poles, *a a a*, at a distance of about 6 inches from the wood forming the back. The space thus left is filled with breeze, which is gently pressed down and continued to be applied until it forms a wall 7 or 8 inches above the piece. Upon this wall is placed a piece of wood, *i*, fig. 9, extending from one side of the pile to the other. A second wall of breeze is built on this wood, and so on until at length the whole of the back of the pile is well coated. These transverse pieces of wood, *i*, are supported by props, *m*, as shown in fig. 9. On the sides of the pile at the bottom, stones about 5 or 6 inches high are laid at intervals, and on these is built up a wall of wood, which is supported by the upright posts, *d d d*, which are firmly stayed by the inclined posts, *d' d' d'*, fig. 10.[6] There should be a clear space of 5 or 6 inches between the inner side of the wall of wood and the sides of the pile formed by the ends of the wood intended for carbonization. This space is filled with breeze simultaneously with the building up of the outer wall of wood. The front of the pile is coated in a similar manner. By means of the stones on the sides and the crosspiece of wood, *h*, at the back, suitable vents may be opened round the bottom of the pile. Care must be taken to stop any openings in the angles at the back, formed by the ends of the transverse pieces of wood which support the cover and the outer side-walls of wood. The pile may now be lighted through the fire-hole, *k*, fig. 10, on the side which at the time may be least affected by the wind, the opposite end being stopped, and kept so for some time after ignition. When the surrounding wood is well kindled, small holes are made from the roof down into the fire-hole, *k*, *successively* along it to draw the fire towards the opposite end, as indicated by the direction of the arrow in the annexed cut. When the fire has reached about one-third of

Fig. 11.

This cut represents the top of the lower end of the pile. The dotted parallel lines indicate the fire-hole, which extends from *k* to the opposite side. The round spots between these lines indicate the openings through the roof or cover.

[6] It will be borne in mind that fig. 9 is not a perspective drawing. The bed on which the pile rests is supposed to be raised above the surrounding ground.

the length of the wood as at s, fig. 11, all the vents on this side, including the fire-hole, are closed. Other similar vents are then made on the opposite side, and these are also closed as soon as the wood on that side is ignited. With dry wood it may require a day to light the pile; but with wood which is not dry, the lighting may occupy a day and a half, or even two days. The object should now be to cause the fire to extend equably through the wood *towards the cover above*, and from thence *forwards* and *downwards* to the bottom of the pile. With this view, immediately after the closing of the end of the fire-hole opposite to that at which the lighting took place, five or six vents are made with a spade crosswise in the cover, near *n*, fig. 10, between the two *middle* posts which support the walls of wood on the sides of the pile. As carbonization gradually advances towards the vents in the cover, it proceeds also towards the bottom of the low end of the pile. Wherever the wood feels loose under foot, on walking over the top, it is a sign that carbonization is completed, and the cover over that part of the pile should be beaten down. Owing to the contraction of the wood by carbonization, the cover gradually sinks to a certain extent; and this sinking should take place uniformly across the pile, from one end to the other, without the formation of any steep ridge or irregular projections. If the wood is dry when stacked, carbonization always goes on better and more easily, and after the lapse of five or six days may have extended to the bottom of the foot or low end of the pile. As soon as the vents in the cover emit light smoke, they should be closed, and others made in the cover at the highest part of the pile; and these must be stopped as soon as the smoke which issues from them presents the same light appearance. The whole cover should then be well stamped down, to check the passage of air through it. Other vents, about 12 or 18 inches apart, are next made along the upper surface of the uppermost transverse piece of wood at the back of the pile; and as soon as light smoke escapes from them, they in turn must be closed, and others made at *y*, fig. 9, along the two or three next underlying transverse pieces of wood, so that two or three rows of vents may exist one above another. Vents are at last made round the bottom of the pile, as well on the sides as at the back under *h*; and when it appears that the lowest stratum of wood is carbonized, all the vents are closed and every part of the pile rendered as impervious to air as practicable. The vents are made with a shovel through the coating of breeze into the twig covering; and sometimes they are made deeper by means of an iron bar. When the charring has extended over the whole pile, the cover is gradually taken off, beginning at the foot, and the charcoal lightly quenched with water. It is then removed to a store-house, where it remains until winter, when the roads become suitable for its transport to the furnaces.

The following modifications of this method of charcoal-burning are described by Karsten and other authors. The wood, sawn into lengths of about 8 feet and uncleaved, is placed transversely so as to form a pile about 24 feet long, increasing in height from one end to the other. The bed may be horizontal or slightly inclining upwards

toward the high end. Fig. 12 represents a side view of a pile partly in section. Immediately upon the bed, which is covered as usual with a layer, several inches thick, of small charcoal, long cleaved pieces or straight branches are laid in the direction of the long axis of the pile, and upon these the wood is placed across at right angles. Thinner and dry pieces should be put at the low end where the pile is kindled. All round the pile, at a distance of about 6 inches, upright posts are driven firmly into the ground, at intervals of 2 or 3 feet. Boards are then fixed on the inside of these posts, and the space between them and the sides and ends of the pile is rammed with moistened breeze. The low end may be about 2 feet high, and the high end about 7 or 9 feet. The pieces are piled without reference to uniformity in size, but the largest should be put towards the high end.

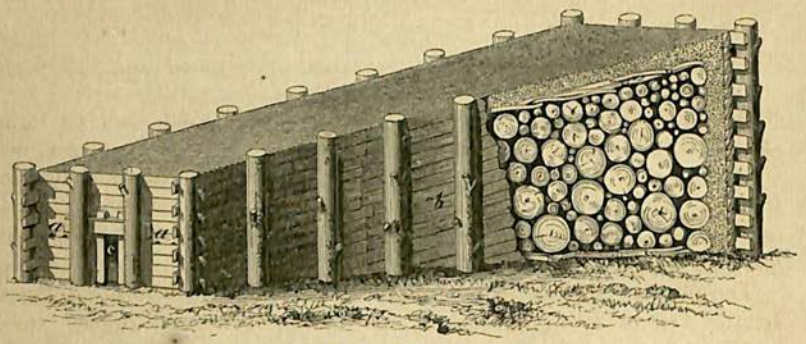

Fig. 12. Copied from Nos. 304 and 305 of Karsten's Atlas. Perspective view, partly in section.

The interstices between the wood should be packed with the small wood of branches. The top of the pile is covered with leaves and faggots, and lastly with small charcoal in the usual way. The pile is ignited at the low end, where a hole *c* is left for the purpose. As soon as light blue smoke escapes from the cover at this end the hole is closed. Three or four holes, an inch in diameter, are then opened through the breeze-coating, about 15 inches from the ground, as seen at *a a*, fig. 12. When, after some time, only light blue smoke makes its way here and there through the cover above, it is a sign that carbonization is so far finished at the low end of the pile that air should be excluded from this part. The holes at *a* are then closed, and three or four fresh ones opened at *b*, 6 or 7 feet farther on, about 2 feet from the ground, and 12 or 15 inches apart, and so the process is carried on to completion. The next holes should be made some inches higher, in proportion to the increasing height of the pile. After the closing of the holes at *a*, two or three fresh ones of the same diameter should be made underneath, quite close to the ground. But these openings ought only to remain open until the appearance of a light scarcely perceptible smoke. When the process has proceeded so far that openings have been made at 8 feet from the high end, charcoal may be begun to be drawn from the low end, when it will rarely be found to be ignited. When the high end of the pile

is actively burning, the charcoal from half of the pile towards the other end should be removed.[7]

7. A pile, similar in form to the last described, is made by placing the wood lengthwise, and inclining upwards towards the high end. Stems which are more than 9 inches in diameter must be cleaved.

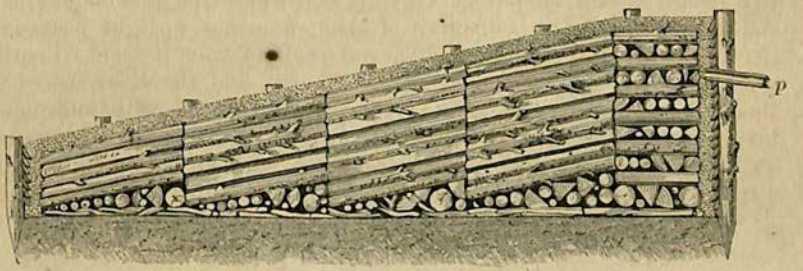

Fig. 13. Longitudinal vertical section. Copied from No. 307 of Karsten's Atlas.

The interstitial space is less than in the last method; and owing to the direction of the wood, combustion is more rapidly propagated through the pile. In large piles of this form, the products of distillation may be collected by inserting cast-iron pipes, *p*, in the high end, and connecting these with a barrel to act as a receiver. The pipes must be kept cool by water flowing over them.

The process of charcoal-burning has been divided into three stages. In the *first* or sweating stage (Schwitzen) desiccation of the wood is effected; one portion of the steam produced escapes through the heated part of the cover, and another condenses and appears especially round the open foot of the pile. The hygroscopic water thus evolved is increased by that derived from the wood in combustion. When this stage is completed, the heat existing in the central and upper part of the pile is sufficient to continue the carbonization of the surrounding wood to a considerable extent; and, accordingly, the supply of air should then be very much reduced by closing, in a greater or less degree, the foot or base of the pile. This constitutes the *second* stage (Treiben). Currents of air are next established successively in various parts of the pile, by making suitable openings at the base, and other openings or vents in the cover above; and so, by a carefully regulated combustion, the wood at the circumference becomes at length converted into charcoal. This is the *third* stage (Zubrennen). Admission of air to every part is then stopped as completely as possible, and the pile is left to itself for a day or so, when the charcoal is withdrawn and extinguished in the manner described.

Chinese methods of charring in pits.[8]—Two methods of making wood-charcoal are practised in China. When the soil is sandy, charring is effected in pits; and when, on the contrary, it is clayey and the

[7] Karsten, Sys. d. Metall. 3. 71 et seq. I have availed myself of Karsten's description condensed as much as possible.

[8] De la fabrication du Charbon de Bois en Chine. Par M. Kovanko, Major au Corps des Ingénieurs des Mines. Annuaire du Journal des Mines de Russie, année 1838, St. Pétersbourg, 1840, p. 375. I have given nearly a literal translation.

locality is suitable, arched chambers are excavated, and in these the wood is carbonized. The last method is preferred by the Chinese, who have carried it to such a degree of perfection that all the small branches and twigs are carbonized without losing their form.

The first method.—The pits are circular, and are never deeper than $1^m 8$ (6 ft.), but they sometimes exceed $4^m 3$ (14 ft.) in diameter.[9] In the annexed woodcuts the pit is shown in vertical section and in plan.

Fig. *a*.

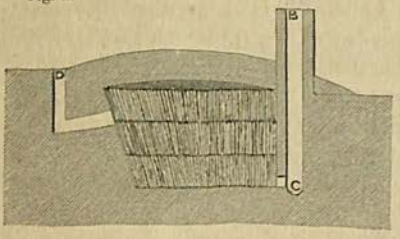

Fig. *b*.

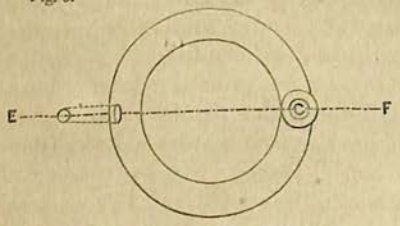

Fig. 14. Chinese Method of Charcoal-burning. Copied from Kovanko's engraving. Fig. *b*, plan of the pit. Fig. *a*, vertical section on the line E F, fig. *b*.

B is a round chimney of which the base is from $0^m 2$ (8 in.) to $0^m 35$ (14 in.) below the bottom of the pit; it rises about $1^m 0$ (3 ft. $3\frac{1}{2}$ in.) above the ground, and is connected with the pit by an oblong opening, C, not exceeding $0^m 35$ (14 in.) in length, and from $0^m 05$ (2 in.) to $0^m 10$ (4 in.) in depth: the dimensions of this opening depend upon the quantity and the size of the wood to be charred. In pits $4^m 27$ (14 ft.) in diameter, the chimney at the base is $0^m 35$ (14 in.) in width, and narrows upwards to $0^m 18$ (7 in.) in width. In that part of the pit which is opposite the chimney is an inclined conical channel, D, from the lower end of which a vertical cylindrical chimney, $0^m 1$ (4 in.) in diameter, rises to the surface. The axis of the conical channel ought to have such an inclination that its lower or narrow end is about equidistant from the bottom and upper edge of the pit. The bottom of the pit is covered with a bed of dry branches, upon which the wood is piled vertically, taking care, as usual, to leave as little interstitial space as practicable. When the pit is filled, the wood is covered first with small branches and then with a layer of soil sufficiently thick to be impervious to smoke. The wood is lighted through the opening opposite the chimney. Occasionally, for the sake of greater facility, a small opening is made above at about $0^m 25$ (10 in.) from the chimney, but which is closed immediately when smoke begins to escape. If the smoke is copious, the pit is covered with stones, a small opening only being left to promote combustion. Five days after lighting the smoke begins to get purer, and when it has become quite transparent the pit and chimney must be hermetically closed. Five or six days suffice for the complete extinction of the charcoal, after which the pit may be opened. Experience in China has shown that the more freshly-cut the wood, the less is the loss: 100 pounds of freshly-cut wood are stated to yield from 30 to 35 of charcoal, which cannot

[9] In reducing the French to English measures I have avoided fractions and given the nearest whole numbers.

possibly be correct. When a large quantity of wood is to be charred, the pits are made wider, but not deeper.

The second method.—The arched chamber excavated in the clayey ground is $1^m 4$ (4 ft. 7 in.) high and $4^m 3$ (14 ft.) wide (see the woodcut, fig. 14). A lateral chimney is formed just as in the first method. In the side of the chamber opposite the chimney there is a conical channel of which the base is directed towards the chamber and extends nearly to the arch, while the narrow end is about intermediate between the bottom and the arch above. The chamber is entered by a low door, which is closed with stones as soon as the charging is completed. The wood is placed horizontally with the usual precautions. The kiln is lighted through the channel opposite the chimney; and when the smoke begins to issue from this channel, it is closed with stones, a very small opening only being left for the passage of the air. At the end of the charring the same course is followed as in the first method.

When a judgment respecting the stage of the process cannot be formed from an examination of the smoke, one or two freshly-cut sticks of the size of the finger are placed across the chimney, and when these sticks, impregnated with oil, are dry and their fracture is black, it is a certain proof that carbonization is ended.

Charcoal-burning in ovens or kilns at Dalfors Iron-Works, Sweden.—I am indebted to my friend Andreas Grill for a description of this process, and the drawings from which the annexed woodcuts have been

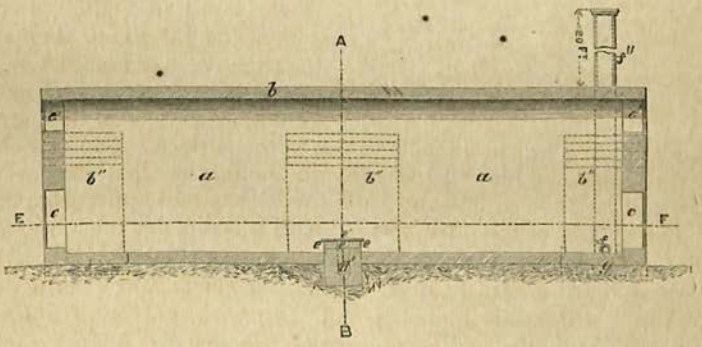

Fig. 15. Vertical Section on the Line C D.

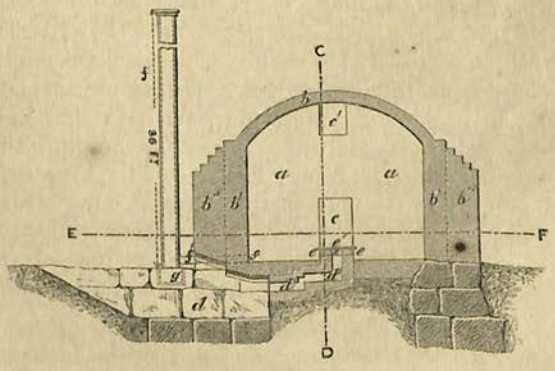

Fig. 16.

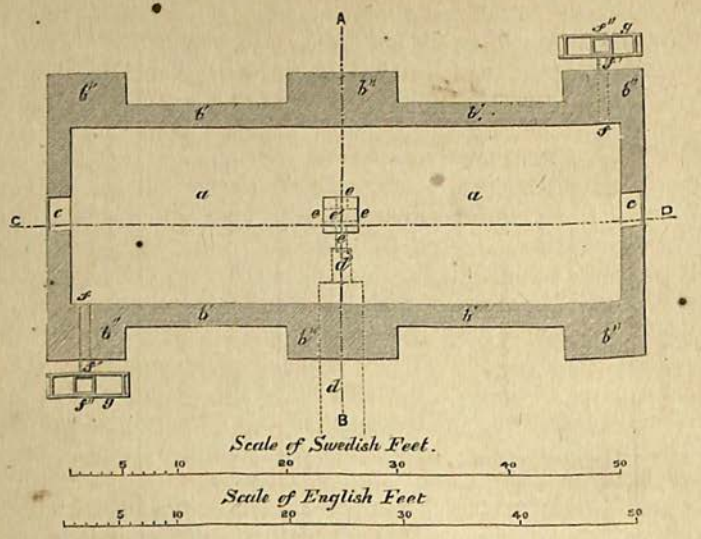

Fig. 17. Plan and Horizontal Section on the Line E F.

executed. The works belong to his brother-in-law, the Hon. W. Didron, who expresses himself well satisfied with the process. *a*, *a*, body of the oven, enclosed above by the arch *b*, *b*, which rests on the side-walls *b'* *b'*, supported by buttresses *b''* *b''*. The oven is filled as closely as possible with layers of wood, first through the lower openings, *c* *c*, and then through the higher ones, *c'* *c'*: these openings are afterwards closed as tight as possible by cast-iron doors, and all fissures are stopped up with clay. During the whole time of charring much care is required to prevent the admission of air through the sides of the kiln. A sunk passage, *d*, leads to the fireplace, *d'*, which is simply a cavity lined with firebricks and without any grate; from the fireplace there proceeds a flue, *d''*, which ends in a cross-flue and communicates with the interior of the oven by four openings, *e*, *e*, *e*, *e*, covered with a cast-iron plate, *e'*. Thus the fire passes immediately to the wood, and the volatile products of carbonization are carried off through the small round openings, *f*, *f*, in the two alternate corners of the oven. These openings are prolonged by iron pipes, *f'*, *f'*, terminating at the bottom of the stacks, *f''*, *f''*, which are provided with sliding dampers, so that, after the completion of carbonization, all connexion may be cut off between the stacks and the interior of the oven. The stacks are made of wooden planks, and stand in wooden troughs, *g*, *g*, filled with water. The condensed tar flows into these troughs, the floor of the oven being made slightly to incline towards the holes *f*, *f*. There is no difficulty in carrying on the process, care being taken to stop up all apertures from which smoke improperly escapes. When the process is terminated, which is indicated by the light colour of the smoke, the fireplace is closed with a cast-iron plate and walled up with brick and mortar. The stacks are also closed, and the whole left to cool.

TABLE SHOWING THE RESULTS OF CHARRING IN OVENS AT DALFORS.

Date.	Charging.			Charring.			Cooling.	Taking out.			General Expenditure.							General Results.		
	Time.	Days' Work.		Time.	Days' Work.			Time.	Days' Work.		Time.	Days' Work.			Total Cost.	Wood consumed in cubic feet.			Yield of charcoal in cubic feet.	Wood required to produce 1 cubic foot of charcoal.	Cost of labour in producing 100 cubic feet of charcoal.
	Days and Nights.	Men.	Horses.	Days and Nights.	Men.	Horses.	Days and Nights.	Days and Nights.	Men.	Horses.	Days and Nights.	Men at 1s. 3d.	Men at 10d.	Horses at 1s. 7½d.		Firing.	Filling of oven.	Total.			
															£ s. d.					Cubic feet.	s. d.
1859. Nov.	1·75	19	..	12·83	25·75	..	14·56	1	6	2	30·14	50·75	..	2	3 0 9	1152	6600	7752	6098	1·27	1 0
1860. May.	2·00	21	4	16·0	32·00	..	37·0	1	6	2	56·00	43·00	16	6	3 18 10	1440	6600	8040	5644	1.42	1 4

Observations.—The horses were employed to draw the wood to the oven and the charcoal to the store-sheds. The better yield was obtained when the wood was dry, and the worse when it was not sufficiently dry.

These results were obtained in an oven exactly similar in construction to, but not so long as, that shown in the woodcut, which is 50 feet long, whilst the other was only 34 feet long. The former is found to work the best. Of the two results given, one is considered only pretty good, and the other very good.

These ovens are not much used in Sweden, and can only be economically employed in peculiar localities, where the works are situated on the banks of a lake or river in the vicinity of a large tract of forest, of which the wood may be readily conveyed by floating.

Yield of Charcoal.—The yield will vary with the nature of the wood, with its age and condition especially as to dryness, and with the mode of conducting the process of carbonization. Of all these causes of variation, the last is the most influential. The yield of charcoal may be computed by measure or by weight. In practice, estimation by measure is usually preferred, because the proportion of water in charcoal is far from constant; and unless special precautions were taken to expel this water before weighing, a very erroneous result might be obtained. But such precautions on the large scale would be impracticable.

In order to ascertain the yield by weight, the data required are simply the weight of the charcoal and the weight of the wood from which it is produced. But if by measure, several methods of computation may be adopted. One German writer enumerates not less than six different modes of estimating the yield of charcoal by measure.[1] One of the most obvious methods, and that which is in use in this country, is to measure the charcoal and the wood, inclusive of the interstices between the pieces, the wood being supposed to be suitably stacked for the purpose. Thus the wood may, according to the usual practice, be estimated in cords, and the charcoal in bushels; and from the data thus obtained, the relation, in cubic feet, between the charcoal and the wood may be readily found. A cord is a pile of wood 4 feet broad, 4 feet high, and 8 feet long; and a bushel is 1·2836 cubic feet. When yield of charcoal by volume is mentioned in this work, the preceding method of computation is referred to, if not otherwise stated. A second method of estimating yield by volume is, to compare the amount of charcoal as determined by measure, *inclusive of the interstices between the pieces*, with the amount of wood, *exclusive of the interstices between the pieces;* in other words, to compare the *apparent* volume of the charcoal with the *actual* volume of the wood. The amount of interstitial space in a closely packed pile of wood, consisting of uncleaved stems, may be taken at about 30 per cent. of the mass; but in the case of cleaved wood or branch wood, this space may be estimated at from 40 to 50 per cent., or even 52 per cent.[2] The statements of different authors do not, as might be expected, exactly agree as to the amount of interstitial space. At Hiflau it is estimated at 25·5 per cent. in wood, and 36 per cent. in charcoal.[3] A third method is to compare the *actual* volume of the wood with the *actual* volume of the charcoal, that is, exclusive of interstitial space both in wood and charcoal. In reading German works on charcoal-burning, it is necessary to remember these differences in the estimation of the yield of charcoal by volume, otherwise much confusion and error may be the result. In some of these works elaborate formulæ are given for the estimation of the cubic contents

[1] Klein, op. cit. 155. [2] Scheerer, Lehrb. 1. 237. [3] Ann. d. Mines, 3. s. 7. 6.

of piles of different forms, but it is presumed that the reader is sufficiently acquainted with the mensuration of solids not to require any special formulæ of this kind.

Yield by Volume.—In Sweden the average yield of charcoal is estimated at 63·2 per cent. of the volume of the wood of Pinus picea and Abies excelsa.[4] The extremes were 50·5 and 75 per cent. Comparative trials have been made in the same country to determine the difference of yield between piles in which the wood is stacked vertically, and those in which it is stacked horizontally. In the former the yield amounted to 67 per cent. and in the latter to 75 per cent. in volume; but these are considered as maxima, the ordinary yield being from 60 to 65 per cent.[5] In Upper Silesia the following yields have been obtained: 52·6 per cent. on the average from stem wood, and occasionally 60 per cent.; 42·7 from branch wood, and 39·5 from root wood.[6] Lampadius states, that in the Saxon Erzgebirge the yield from the stem wood of Pinus picea, in the best managed charcoal burning in round piles, is as much as 80 per cent. in volume.[7] At Hiflau, Styria, the yield from long piles of firwood was found to be 76·8 of large charcoal, and 2·7 of small, making a total of 79·5 per cent. in volume.[8] At the same place the yield from large round piles has reached 86·2 per cent.[9] In some cases the volume of charcoal is stated to have exceeded that of the original wood even to the extent of 28 per cent.

The discordancy between these results is so great, that it cannot be attributed to the causes of variation previously mentioned; it must be due either to error of observation, or to a variable or fallacious method of computation; and that the latter may in some instances have been the true cause, will appear from the following remarks. The volume of the wood may have been deduced from the cubic contents of the pile as determined by admeasurement. Now the amount of interstitial space may vary greatly in different piles, not only with the degree of compactness with which the wood is stacked, but also the size and irregularity in shape of the pieces. The amount of the space, as Karsten remarks, could only be correctly determined by filling the interstices with sand, and afterwards measuring its volume; but no such determination seems to have been made, at least on a large scale. In respect to the volume of charcoal, the amount of interstitial space may vary considerably, especially from the greater or less degree of splitting in the wood during carbonization. When the wood is not sufficiently dry, splitting may take place to a very sensible extent; and probably in this way the statement that the volume of charcoal has, in some cases, exceeded that of the original wood, may be explained. We know certainly that wood contracts sensibly in all dimensions by carbonization, and in length from 11 to 12 per cent. Cork, however, which is bark and not wood, increases in volume by

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[4] Af Uhr, Scheerer, Met. 238. Mr. Grill of Sweden confirmed this statement to the author.

[5] Durocher, Ann. d. Mines, 5. s. 9. 363.

[6] Wittwer, Karsten's Archiv, 2. r. 24. 293.

[7] Hüttenkunde, 1827, 48.

[8] Ann. d. Mines, 3. s. 7. 6. The species of fir is not stated.

[9] Op. cit. 18.

carbonization.[1] The degree will depend upon the kind of tree, its age, the part of the tree, and other circumstances. Young wood and branch wood contract more than old or mature wood and stem wood. In general, coniferous wood contracts less than other wood. Fir wood, when young and soft, loses from 46 to 47 per cent. in actual volume by carbonization, but when old and strong at least 44·5 per cent. In the case of non-coniferous wood, the hard kinds contract considerably more than the soft: the young wood, the branch wood of the softer kinds, and the harder kinds of wood, lose 52 per cent. in volume, whereas the mature wood of the softer kinds loses only 50 per cent. A yield of 55 per cent. in volume from coniferous wood, and 48 per cent. from non-coniferous wood, may be regarded in general as favourable.[2]

Yield by Weight.—The yield, by *weight*, of charcoal has been often determined; but as might be expected, there is great discrepancy in the results which have been published on the subject. Various causes influence the yield in a marked degree, so that unless the precise conditions under which the charring has been effected are stated, the observations of one author cannot well be compared with those of another. The weight, however, may be considered as ranging between 15 and 28 per cent. of that of the wood. In different localities in the north-east of France, the yield from circular piles, containing from 60 to 90 cubic metres of wood, has been found to range from 17 to 21·33 per cent. in weight.[3] The kinds of wood employed were beech, oak, poplar, willow, and hornbeam. It is estimated in France, that with good charcoal burners an average yield of not more than 19 per cent. should be calculated on.[4] In Belgium, from wood of 15 to 20 years' growth, a yield of 15 to 17 per cent. is obtained; and if the charring be slowly conducted, it may amount to 20 or 22 per cent. at the most. The wood employed consists of $\frac{3}{4}$ to $\frac{3}{4}$ of the hard kinds.[5] In Sweden, the yield from Pinus sylvestris and picea by charring, in rectangular piles, has been found, according to Af Uhr, to range from 20 to 28 per cent.[6] A yield of 22 per cent. in weight may be regarded as very favourable.[7] The average yield of twenty-six recorded observations on charring in piles in different localities is, in round numbers, 23 per cent., the extremes being 19·5 and 28·0.[8] By carbonization on the large scale, in iron vessels, heated from without, Lampadius obtained a yield, from air-dried Pinus picea, of about 27 per cent. in weight.[9] The author is indebted to his friend and former pupil Mr. C. B. Hambly, who is engaged in the manufacture of pyroligneous acid, for the following information on this subject. The wood used consisted of three-fourths oak and one-fourth of mixed beech, ash, &c., and the distillation was effected in retorts 3 feet 6 inches wide and 5 feet long. The yield

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[1] Karsten, Eisenhüttenkunde, 2, 267.
[2] Karsten, op. cit. 2, 268.
[3] Sauvage, Ann. d. Mines, 3. s. 11. 359.
[4] Tr. de la Fabrication de la Fonte, &c. Par Flachat, &c. Part 1. 112.
[5] Valerius, Tr. Théor. et Prat. de la Fabric. de la Fonte, 232. 1851.
[6] Op. cit.
[7] Karsten, Eisenhüttenkunde, 2 part. 286.
[8] Scheerer, Lehrb. 1. 236.
[9] Grundriss einer allgem. Hüttenkunde, 1827, p. 48.

in weight varied from 25 to 27 per cent.; it was deduced from the distillation of 328 tons 6 cwt. of wood.

Influence of Temperature upon yield.—Numerous experiments by Karsten have proved that the more slowly—or what is equivalent, the lower the temperature at which—the charring is effected, the greater will be the yield. The following Table contains his results.

100 parts by weight of the following kinds of wood gave of charcoal	By rapid charring.	By slow charring.
Young oak	16·54	25·6
Old do.	15·91	25·71
Young beech (Fagus sylvatica)	14·875	25·875
Old do.	14·15	26·15
Young hornbeam (Carpinus Betulus)	13·12	25·22
Old do.	13·65	26·45
Young alder (Alnus glutinosa)	14·45	25·65
Old do.	15·3	25·65
Young birch	13·05	25·05
Old do.	12·2	24·70
Birch of a post which had stood over a grave above 100 years, and was yet sound	12·15	25·1
Young Pinus picea	14·25	25·25
Old do.	14·05	25·0
Young Abies excelsa	16·225	27·725
Old do.	15·35	24·75
Young Scotch fir (Pinus sylvestris)	15·52	26·07
Old do.	13·75	25·95
Lime (Tilia Europæa)	13·33	24·60
Rye straw	13·4	24·60
Dried fern	17·0	27·95
Reeds	14·65	26·45
Mean	14·42	25·69

The wood operated on in these experiments had been previously well air-dried.[1] Karsten's results have been confirmed by Violette.[2] Ebelmen has determined the effect of rapid carbonization upon *green* and *dry* wood respectively.[3] His conclusion is, that the yield of charcoal from *dry* wood, as compared with *green*, is in excess proportionate to the degree of desiccation. Ebelmen also found, that when different weights of the same wood, in the same state of desiccation, are exposed to a constant temperature in vessels of the same nature and the same capacity, the proportion of charcoal obtained increases up to a certain limit with the weight of wood operated on.

Illustrative results of charcoal-burning in piles.—The following Table has been compiled by Beschoren from actual results. In the first column the yield is estimated by weight; in the second column it is stated according to the method of computation by measure first described; and in the third column it is stated according to the second method of computation.

[1] System. 3. 34. [2] Ann. de Ch. et de Phys. 3. s. 32. 315. 1851.
[3] Recueil des Trav. Scient. 2. 178.

		Yield of charcoal.		
		Weight from 100 of wood.	From 100 cubic feet of wood in apparent volume.	From 100 cubic feet of wood in actual volume.
1.	Oak	21·302	71·842	98·672
2.	Do.	23·447	74·299	102·009
3.	Beech	22·661	73·029	100·369
4.	Birch	20·945	68·518	94·189
5.	Hornbeam	20·575	57·197	78·584
6.	Scotch fir (Kiefer)	25·029	63·561	87·157
	Mean	22·355	68·195	93·645

The charring was effected in piles in which the wood was stacked vertically, in either two or three layers; and all the observations seem to have been made with great care at Eisleben, under the immediate direction of Beschoren, who styles himself charcoal manufacturer.[4] The oak and beech were from trees 150 to 200 years old, the birch and hornbeam from 50 to 60, and the fir from 70 to 80.

The following summary of the actual results obtained by Beschoren may be interesting in a practical point of view, as showing the time required to effect the charring of given quantities of wood in piles. The numbers in the first column correspond to those in the first column of the last Table.

No.	When lighted.	When cooled.	Duration of charring process.	Weight in pounds Prussian.[5]			
				Weight of Wood.	Wood consumed in filling the pile from time to time to be deducted.	Actual weight of wood from which the charcoal was derived.	Yield of charcoal.
			Days.				
1	Sept. 4	Sept. 16	13	68035	120	67915	14467
2	„ 7	„ 20	14	67595	205	67390	15801
3	„ 1	„ 12	12	47685	102	47583	10783
4	Aug. 30	„ 12	14	47630	. .	47630	9976
5	„ 7	Aug. 17	11	52470	80	52390	10780
6	Sept. 27	Oct. 15	19	55660	1983[6]	53677	13435

The weather was unfavourable during the charring of No. 6. Too much air entered the pile, owing to the dryness of the ground. The large yield is to be explained by the fact that the wood was much drier than that charred in the preceding experiments. In No. 5 the wood was not nearly so dry as in the first four experiments. The *apparent* volume of wood operated on ranged from 1149 to 2025 cubic feet (Prussian), and the *actual* volume from 836·02 to 1476·77 cubic feet.

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[4] Versuche über das Ausbringen an Holzkohlen aus verschiedenen Holzsorten. Bergwerksfreund, 3. 1. 1840.

[5] 1 pound Prussian = 1·031 pound avoirdupois.

[6] This includes a considerable amount of brands, *i. e.* imperfectly carbonized pieces.

Summary of practical directions in charcoal-burning.—The wood should be of mature growth, neither too old nor too young. It should be felled when most free from sap, that is during winter. It should be partially or wholly barked and air-dried for some months before burning. Experience teaches that the best result is obtained when the wood is moderately dry. If too dry, the combustion is too quick, and not easily regulated by the charcoal-burner, carbonization proceeds irregularly, charcoal is uselessly consumed, and as a consequence its quality is injured, and the yield diminished. In this case the pile must be as flat as practicable, and the cover must be made thicker and more dense, so as sufficiently to reduce the supply of air to the pile. If, on the other hand, the wood is too moist, the process is considerably prolonged, more care and labour are required, but the charcoal produced is sounder and of better quality than in the last case. The steam must be allowed freely to escape, by either partially removing the cover, or diminishing its thickness and solidity at the upper part during the sweating stage.[7] Rotten and worm-eaten wood should be avoided, as the charcoal from it is so bad as to be unfit for smelting. By long exposure to the action of water, whether by floating down rivers or remaining unprotected from heavy rains, wood is sensibly deteriorated for charcoal-burning. Immersion, however, during ten days or a fortnight occasions no injurious effect.[8] If the ground on which the bed is made is too porous, too much air may find its way into the interior, and so cause unnecessary waste of charcoal. In this case the bed should be rendered less pervious to air by making it more solid; and when practicable, by covering it with a layer of the residual charcoal dust from previous burnings. A clayey ground is bad, as it may become fissured by the heat evolved in the process; and the fissures may serve as channels for the admission of air, when the same evil would occur as in the last case. In moist ground, a foundation of wood covered with soil should be first laid, and on this the pile should be raised. If a sheltered situation cannot be found, the pile must be protected from wind by hurdles or other suitable expedients. Exposure to wind will obviously tend to prevent regularity in burning. Any hollow spaces caused by the burning away of the fuel used in lighting the pile should be replenished with wood or charcoal, or the imperfectly charred pieces from previous burnings, or a mixture of both, which should be pressed well in by means of a pole; and the surface of the pile should be sounded from time to time, to ascertain if hollows exist. Any fissures which may appear in the cover should be stopped. There is nothing fixed in respect to the dimensions of piles; they vary in diameter from 10 feet to 50 and upwards. Most frequently the diameter is from 20 to 30 feet. In height they vary from $\frac{1}{3}$ to $\frac{1}{2}$ of the diameter measured at the base.[9]

Charcoal should not be used in blast furnaces or forges immediately after burning, as it has been found to improve by keeping at least

[7] Helmest, Erdmann's Journ. 4. 230. [8] Af Uhr, op. cit. 11.
[9] Scheerer, Lehrb. 1. 221.

during several months. With the same charge of ore and flux in an iron smelting furnace, the same quantity of freshly burnt charcoal was found to be less effective than charcoal which had been kept during two years well under cover.[1]

Theory of charcoal-burning in circular and rectangular piles.—From the mode of conducting the process of charcoal-burning in piles, it might be inferred that the combustion is propagated from above downwards, and from the centre to the circumference. Ebelmen has given an experimental demonstration of this fact.[2] A pile containing 30 cubic metres (1059 cub. ft.) of oak, beech, and fir, in pieces 0^m 70 long (2 ft. 4 in.), was made in the usual way. In the centre was a chimney 0^m 25 (10 in.) in diameter, extending from the bottom to the top of the pile, and around it the wood was stacked in three rows, one above another; the large pieces being placed in the centre and the small outside. The diameter of the pile was 7 metres (22 ft. 11½ in.), and the height about 2 metres (6 ft. 7 in.). It was covered all over as usual with soil and breeze. It was lighted in the morning by putting ignited charcoal into the chimney, which was left open for some hours. Vents were made all round the bottom of the pile, and remained open during the whole process, to supply air for the combustion. When the pile was sufficiently ignited, the chimney was filled with small wood and then closed. In the evening the vacant space caused by the burning away of the wood in the chimney was filled with breeze. This was again done next morning. In the course of the day vents were made in the covering of the pile near the top. The smoke which escaped from them was white, thick, and copious; but after some hours it became bluish, almost transparent, and much less abundant; when the charcoal-burner made fresh vents, about 20 (8 in.) or 25 (10 in.) centimetres below those above. On the third day, when the vents were 1^m 20 (3 ft. 11½ in.) above the ground, half of the pile was removed, and the ignited wood and charcoal were extinguished with water. The annexed diagram shows

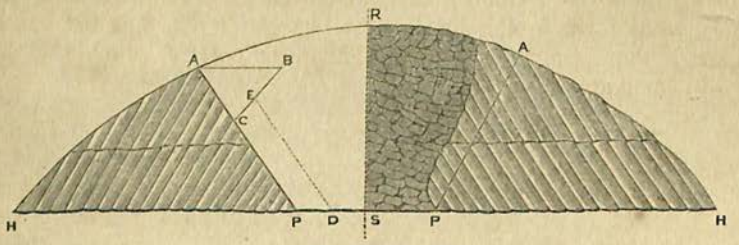

Fig. 18. Copied from Ebelmen's figure.

the condition of the pile at this time. The charcoal was all contained within the space produced by the revolution of the plane A R S P round

[1] Karsten, Sys. 3. 45.

[2] Recueil des Travaux Scientifiques de M. Ebelmen, 2, p. 104 et seq. I have as far as practicable literally translated Ebelmen's language.

the axis R S. This space represents nearly an inverted truncated cone, of which the radius of the small base next the ground is about 0^m 40 (1 ft. 4 in.). In the rest of the pile the wood was unchanged, the pieces being only blackened on the surface by tar, and exhaling an empyreumatic odour; on sawing them across it was evident that they had not even begun to undergo desiccation. The greater part of the charcoal contained within the space A R S P was in pieces placed irregularly as in a heap of charcoal, and without any connection with the surrounding wood. It was only in that part of the pile corresponding to the triangle A B C, and the space included between the line A P and the parallel line E D, by their revolution round R S, that the charcoal remained attached to the wood. The distance between D E and A P was from 10 (4 in.) to 15 (6 in.) centimetres. On each of the pieces of wood included within A P, the passage from perfect charcoal to unchanged wood might be traced, the two being separated by partially carbonized brown wood to the distance of 7 (2¾ in.) or 8 (3 in.) centimetres. The carbonized part of the wood had undergone very sensible contraction. If carbonization had been allowed to proceed unchecked, the angle H D E would have continued to decrease, until at length the line D E would have coincided with H D, and then all the wood would have been converted into charcoal. Hence it is clear that carbonization in piles is propagated from above downwards, and from the centre to the circumference.

The air enters at the bottom of the pile, and finds its way to the space within A P, to which combustion is limited; and the volatile products of carbonization escape at the vents A B, round the upper part of the mound. It is in this space that the charcoal last formed remains attached to the wood. But as the volume of charcoal is considerably less than that of the wood from which it is produced, the spaces between the carbonized parts of the pieces of wood must be considerably greater than between those which remain uncarbonized. Moreover, within the line E D the charcoal is detached, broken, and irregularly piled in a heap. Hence, the circulation of air should take place most readily where the least resistance is offered, that is, upwards through the space C E D P, with the upper part of which the vents are in communication.

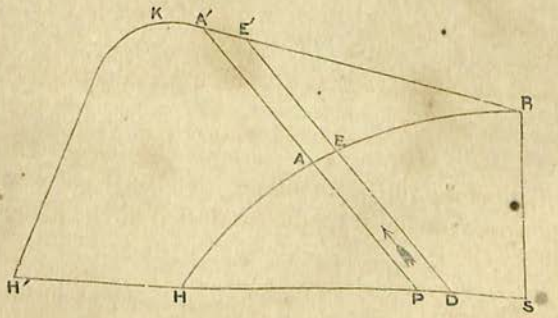

Fig. 19.

In the rectangular pile the process of carbonization would appear to take place in much the same manner as in the circular pile. In the preceding diagram, fig. 19, let R H S represent the left half of the vertical section of a circular pile (see fig. 2, *a*), and let R K H′ S represent the vertical section of the rectangular pile, fig. 8. Now in the circular pile carbonization commences along the line R S and proceeds outwards and downwards in the direction of the line E D. Suppose the wood within the space R E D S to be already converted into charcoal, and the process of carbonization to be active within the space E A P D, the air by which combustion is sustained circulates upwards in the direction of the arrow. But this is certainly the direction in which the air circulates through the rectangular pile R K H′ S. In the circular pile the smoke escapes through vents all round on a level with A; whereas in the rectangular pile it escapes through vents across the top at A′.

According to Ebelmen, the heat by which carbonization is effected in piles is produced solely by the combustion of charcoal already formed, and not in any degree by the combustion of the volatile products evolved. He analysed the volatile products which issued from the vents of piles in different stages of combustion, and those which are produced by the carbonization of wood in *close* vessels. In the case of the pile, the permanent gases will contain all the nitrogen of the air which has contributed to sustain combustion, together with an amount of carbonic acid corresponding to the oxygen of that air; that is, admitting that the oxygen is wholly converted into carbonic acid by contact with the ignited charcoal of the pile. Now, if we deduct from these permanent gases all the nitrogen, and an amount of carbonic acid containing oxygen, proportionate to the amount with which nitrogen is associated in atmospheric air, the residual gases will be found to approximate in composition to the permanent gases produced by the carbonization of wood in close vessels. The following experimental results in proof of this were obtained by Ebelmen.

COMPOSITION OF PERMANENT GASES FROM PILES.

	1.	2.	3.	4.	5.	6.	7.	8.	9.
Carbonic acid	25·57	26·68	27·23	25·89	28·34	21 26	23·51	23·28	23·08
Carbonic oxide	8·68	9·25	7·67	9·33	15·17	5·18	5·00	5·88	6·04
Hydrogen	9·13	10·67	11·64	9·28	8·87	8·84	4·89	13·53	14·11
Nitrogen	56·62	53·40	53·46	55·50	47·62	64·72	66·60	57·31	55·77
	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00

COMPOSITION OF THE GASES AFTER DEDUCTION OF THE NITROGEN AND CORRESPONDING CARBONIC ACID.

	1.	2.	3.	4.	5.	6.	7.	8.	9.
Carbonic acid	37·5	38·8	40·3	37·8	39·7	23·5	37·8	29·8	29·6
Carbonic oxide	30·4	28·4	23·6	31·2	38·0	28·2	31·4	21·2	21·1
Hydrogen	32·1	32·8	36·1	31·0	22·3	48·3	30·2	49·0	49·3
	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00

(1.) Gas from the vent of a pile, at one-third of its height, two days after lighting. The pile contained 60 cubic metres (2118 cub. ft.). The vent had been opened 6 hours before, and gave much thick white smoke. A mercurial thermometer put in to the depth of 0^m 10 (4 in.), and taken out after 8 minutes, marked 260° C. (2.) Gas 24 hours after No. 1, from a vent in the same pile, opened an hour previously. There was much dense white smoke. (3.) Gas 24 hours after No. 2, from a vent in the same pile, at 0^m 60 (1 ft. 11½ in.) from the ground, opened an hour before. There was much white smoke. Temperature 230° C. (4.) Gas from a vent of another pile containing 35 cubic metres (1235½ cub. ft.), at 0^m 60 (1 ft. 11½ in.) from the ground, 4 days after lighting. Much dense white smoke issued from this vent. (5.) Gas from the same pile as No. 4, at 0^m 30 (11¾ in.) from the ground, and 18 hours before the termination of the burning. Dense white smoke. (6.) Gas from the vent of another pile, 0^m 60 (1 ft. 11½ in.) from the ground and 36 hours before the termination of the burning. Smoke bluish, transparent, and not copious. (7.) Gas from the same pile as No. 1, 18 hours afterwards. The vent was 0^m 30 (11¾ in.) below those from which gas No. 1 issued, and was made 4 hours previously. White and not very dense smoke. (8.) Gas from the same vent as No. 7, but 5 hours afterwards. Smoke clear and slight. Temperature 250° C. (9.) Gas from the same pile as No. 8, 24 hours afterwards; the smoke which issued from the vent was slight, bluish, and almost transparent. The piles employed in these experiments were constructed like that described under No. 4 (p. 115).

Composition of Permanent Gases by Carbonization in Close Vessels.

	10.	11.
Carbonic acid	44·9	29·2
Carbonic oxide	36·8	24·9
Hydrogen	16·8	44·2
Nitrogen and loss	1·5	1·7
	100·00	100·00

The wood was subjected to distillation in a small iron retort heated to cherry-redness. (10.) Gas half an hour after the retort was put into the furnace. Thick, white, irritating, and non-inflammable smoke issued. (11.) Gas 1½ hour after the beginning of the carbonization; it burnt spontaneously with a blue flame as it issued from the retort.

It will be observed that in both methods of carbonization the proportion of hydrogen greatly increases towards the end of the distillation, while, at the same time, the carbonic acid and carbonic oxide decrease. At the end of the carbonization, in both cases, the composition of the permanent gases is very similar.

Ebelmen made three determinations of the amount of condensable matter evolved during carbonization in piles, and one of the amount produced by distillation in a retort. For 1 litre (61·02 cub. in.) of

dry gas reduced to 0° C. and 0m 760 bar., the weight in grammes was as follows :—

	In a pile.			In a retort.	
	grammes.	grains.		grammes.	grains.
1.	0·987	15·232	4.	2·812	43·395
2.	1·068	16·481			
3.	0·531	8·194			

(1.) From a vent 1 metre (3 ft. 3½ in.) above the ground, opened an hour before; smoke dense and white. (2.) From a vent on the same level as (1), and 45 minutes afterwards. (3.) From a vent 1 metre above the ground. Smoke bluish and almost transparent, carbonization being far advanced in this part of the pile. (4.) Collected immediately after the gas in (11) p. 137.

In order properly to compare these results of carbonization in piles and retorts, those analyses of the volatile products produced during similar stages of the process should only be selected. Ebelmen accordingly takes the mean of the first five analyses of the permanent gases, and the mean of the first two determinations of the amount of condensable products evolved during carbonization in piles. The following Table will facilitate the comparison in question.

	Products of the carbonization in a pile.	Products of the carbonization in a retort.	
Carbonic acid	39·0	mean of (10) and (11)	37·5
Carbonic oxide	30·6		30·8
Hydrogen	30·4		30·5
	100·0		100·0
Weight of liquid products condensed in collecting 1 litre (61·02 cub. in.) of dry gas, reduced to 0° C. and 0m 760 bar. in the first column, calculated after the deduction of the nitrogen and carbonic acid corresponding to the oxygen existing with the nitrogen in atmospheric air.	3 grms 142 (48·487 grs)	..	2 grms 812 (43·395 grs)

From the preceding data it would appear that the average composition of the permanent gases produced during carbonization in piles and retorts is similar, though not identical. But this similarity of composition is only obtained by taking the mean of the two analyses (10) and (11) of the gases from the retort, which were very dissimilar, especially in the proportion of hydrogen. Even on this ground alone it may be questioned whether the conclusion of Ebelmen, that the heat by which carbonization in piles is effected is produced exclusively by the combustion of carbon, is sufficiently proved. The evidence in favour of that conclusion, derived from a comparison of the liquid products, is still less satisfactory; and even if the similarity were greater than it is, a confirmation of the results would be required to justify any decided inference from them.

The method of analysis which Ebelmen adopted is incorrect. He passed the gases through a red-hot tube containing oxide of copper, and

weighed the carbonic acid and the water produced, as in an ordinary organic analysis; and by this method no evidence would be afforded of the presence of carburetted hydrogen, which recent investigations have proved to be a constituent of the permanent gases evolved during the dry distillation of wood. When wood is heated to the temperature of boiling mercury, it is carbonized, and the gases produced are composed as follows, exclusive of about 5 per cent. of atmospheric air.

Carbonic acid	54·5
Carbonic oxide	33·8
Marsh gas	6·6

If the volatile products from the carbonization of wood be subjected to a considerably higher degree of heat, a large amount of olefiant gas may likewise be generated; and hence the successful application of these gases to the purpose of illumination. Their composition has been found to be as follows:—

	Per Cent.
Carbonic acid	18 to 25
Carbonic oxide	40 to 50
Hydrogen	14 to 17
Marsh gas	8 to 12
Olefiant gas	6 to 7

The volatile products, condensable as well as permanently gaseous, evolved from different kinds of wood, such as beech and fir, have essentially the same composition.[3]

It has been previously stated that ordinary charcoal retains a sensible amount of hydrogen (p. 109), and if such charcoal be burnt, it is impossible to conceive that during the process of charcoal-burning the carbon alone should be consumed, and the hydrogen wholly escape combustion. Indeed, Ebelmen himself has mentioned this objection, but remarks that it does not at all alter the conclusions which he has drawn from his experiments.[4]

But admitting that Ebelmen had established that the gases from piles and retorts were, after deducting the nitrogen and carbonic acid as above mentioned, identical, still, as Scheerer remarks,[5] it would not follow that carbonization in the former is due solely to the combustion of charcoal. In order to justify that conclusion, it must be shown that the nature and amount of condensable or liquid products are the same in both cases. It is, however, manifestly impossible to collect all the liquid products from a pile, as may be done from a retort; and that no decided conclusion can be drawn from the relation between these products and the permanent gases of piles,—abstraction made of the nitrogen and of carbonic acid proportionate to the oxygen with which it exists in atmospheric air,—is clear from Ebelmen's own examination of a pile in process of carbonization. In that examination, it will be borne in mind, tarry matter was found condensed on the unchanged and partially charred wood. There is, therefore, no proof

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[3] Jahres-Bericht. Wagner. 1858, p. 473.

[4] Recueil des Trav. Scient. 1855, 2, p. 123, in a note.

[5] Lehrb. d. Metall. p. 251.

from Ebelmen's experiments that the amount of tar from piles and retorts is the same. It is true that the same amount of tar may be generated in both cases; but in the absence of proof, it cannot be admitted that in piles no tar is subsequently burned. By the perfect combustion of tar much heat may be developed, the products being carbonic acid and water. Now Scheerer explains how he conceives the composition of the permanent gases from piles,—exclusive of the nitrogen and carbonic acid of which the oxygen has been derived from the air,—may be the same as that of the gases from retorts; notwithstanding that in piles the volatile products may be partially burned. His explanation is as follows: let it be granted that the relation between the gaseous and liquid products may, at the moment of their development, be the same in piles as in retorts. Suppose, then, that a portion of the volatile products of piles is partially burned by the action of atmospheric air; and let us exclude from consideration any carburetted hydrogen which may be present. The products of such combustion would be *carbonic acid* from the *carbonic oxide*, *water* from the *hydrogen*, and *carbonic acid* and *water* from the *tar*. The original quantity of carbonic acid and water would, consequently, be increased; while, on the contrary, that of the carbonic oxide, hydrogen, and tar would be diminished. It is certain that a portion of the previously formed charcoal is burned, and with the production, most probably, of carbonic acid, so that an addition of this gas would be made to that originally formed. It is inconceivable that all the carbonic acid and vapour of water should be exposed to the action of the ignited charcoal of the pile, and yet that none of the former should be converted into carbonic oxide, and none of the latter into carbonic oxide, carbonic acid, and hydrogen. Hence, from one source there would be an *increase*, and from another source a *decrease*, in the quantity of carbonic acid, and an increase in that of the carbonic oxide and hydrogen. It appears, therefore, probable, from the preceding data, that a considerable proportion of the volatile products of piles may suffer combustion, and yet the permanent gases which escape from them,— exclusive of those derived from atmospheric air,—may only differ from the volatile products of retorts in containing a larger amount of carbonic acid, and in being accompanied with a smaller amount of tar. We may thus understand how the oxygen of the *excess* of carbonic acid in the gases of piles may have the same relation to the nitrogen as exists between these gases in atmospheric air. This relation must be exactly preserved if as much carbonic acid be produced by the action of the vapour of water on the ignited charcoal as there is of carbonic acid converted into carbonic oxide by the action of the ignited charcoal.

However plausible Scheerer's objections to Ebelmen's theory may at first sight appear, it must yet be borne in mind that they do not rest on experimental evidence. In order that carbonic acid should be converted into carbonic oxide by contact with ignited carbon, it is necessary that the temperature should be much higher than that of mere ignition; but whether that degree of temperature exists in piles is not shown. But admitting that it does exist, then, in the case of the

conversion of any carbonic acid into carbonic oxide, as much heat will be absorbed for every equivalent of carbonic oxide so produced as was evolved by the combination of the second equivalent of oxygen in the original formation of that carbonic acid. If, therefore, on the assumption of the partial combustion of the gaseous products in charcoal-burning, as much carbonic oxide is reproduced by the action of incandescent charcoal on carbonic acid as is burned and converted into carbonic acid, nothing is gained, or, in other words, there is no addition of heat from such partial combustion of carbonic oxide. This is equally true in respect to the partial combustion of the hydrogen, provided as much hydrogen is reproduced by the action of incandescent charcoal on the vapour of water as was burned. If it were not so, there would be a positive generation of heat; or what is equivalent, a creation of force, which is impossible.

Supposing that there is perfect combustion of a portion of the tar produced in piles, it is easy to conceive how there may be identity between the composition of the permanent gases evolved from retorts and piles respectively,—that is, after the deduction from the gases of piles of all the nitrogen and the excess of carbonic acid corresponding to the proportion of oxygen derived from the atmosphere; for as the products of the perfect combustion of tar are carbonic acid and water, that excess of carbonic acid may as well be derived in part from the combustion of tar as from the previously formed charcoal. The amount of water, it is true, would be increased by the combustion of tar, and by so much would the volatile products of piles exceed those of retorts; but no facts have been adduced to show that the proportion of water from piles and retorts, *cæteris paribus*, is the same.

Scheerer has further attempted to oppose the theory of Ebelmen by proving that the amount of heat developed by the combustion of charcoal alone is far from sufficient to determine carbonization in piles; and if his datum be granted, that only 3 per cent. of charcoal is actually burned, his ground of opposition is fatal to the theory in question. However, in many recorded observations concerning the yield of charcoal by burning in piles, it is certain that much more than 3 per cent. has been consumed. As the evidence advanced on both sides is defective in scientific precision, probably the best course is to suspend judgment, and to admit that, while Ebelmen has failed conclusively to establish his theory, Scheerer has also failed satisfactorily to overthrow it.

Cost of charcoal-burning in circular piles.—The cost will obviously vary with the price of labour in different localities, irrespective of the price of wood. By way of illustration I insert the following details of the present cost of charring in circular piles at the well-known iron-works and gun-foundry at Finspong in Sweden. The information has been kindly supplied by the manager of the forests through Andreas Grill (July, 1861). All the labour is contracted for, and is arranged under the three following heads :—

	s.	d.
1. Felling, chopping off the branches, and preparing the wood, per 100 Swedish cubic feet charcoal	0	6½
2. Conveying the wood to charring-place, by horse-labour	0	6¾
3. Piling the wood, covering the pile, charring and quenching or damping	1	1½
Total	2	2¾
Ditto per 100 cub. ft. English[6]	2	4¾

A man is calculated to earn from 11*d.* to 1*s.* per day; and a horse with driver 2*s.* 6*d.* per day.

The cost of charring in rectangular piles is slightly greater.

Peat Charcoal or Coke.

The attention of metallurgists has long been directed to the preparation of charcoal from peat, with a view to its substitution for charcoal from wood. In 1727 a patent was granted to William Fallowfield for the use of charred peat in the smelting and manufacture of iron.[7] Previously, in 1712, Carlowitz mentions the fact that peat was charred in circular piles or stacks, in the same manner as wood.[8] According to Vogel, peat charcoal was made in the Harz in 1735, and applied with success on a large scale in metallurgical operations; but this application was disparaged by one class of persons simply on account of its novelty, and by another class who were interested in keeping up the price of wood. It was even maintained that peat charcoal was unsuited to the smelting and manufacture of iron, because it evolved an acid vapour which would attack the metal and injure its quality.[9] But neither prejudices nor interested opposition, however strong, could long have prevented its use in metallurgy, if it had not been found inferior in some respects to other kinds of fuel. The quality of the charcoal will obviously vary with the quality of the peat from which it is prepared. It will be light or dense according as it is derived from fibrous or compact peat; but the charcoal obtained from any kind of peat is stated to be tender and incapable of supporting moderate pressure without crumbling. This defect alone would render it unsuitable as fuel in ordinary blast-furnaces, in which the contents are subjected to considerable pressure. If, however, peat be carbonized after having been much reduced in bulk by compression, the charcoal is in great measure free from this defect; but then the preliminary process of compressing the peat may increase the cost of the charcoal to such a degree as to prevent its profitable application in metallurgical operations. During some years the subject of peat charcoal has received much attention from the practical metallurgists on the Continent. Various methods of manufacturing it have been tried, and the results of its use in blast

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[6] 108 c. f. Swedish = 100 c. f. English.

[7] Abridgments of the Specifications relating to the Manufacture of Iron and Steel, 1857, p. 3.

[8] Vogel, op. cit. p. 105.

[9] Op. cit. p. 105.

and other furnaces recorded; but as these results are not a little conflicting, some being favourable and others unfavourable to its use, further evidence is required to enable us to arrive at a satisfactory conclusion on the matter.

Peat charcoal may be prepared by methods exactly similar in principle to those employed in the carbonization of wood. Kilns of various kinds have been constructed for the purpose, but I shall not give any description of them, as I do not at present consider the subject of sufficient importance to the practical metallurgist. When the charring of peat is effected in kilns by the heat resulting from the combustion of a portion of the peat, it is recommended to conduct the carbonization from above downwards, just as in the coking of coal in ovens.[1] When peat is charred in circular piles like those employed in making charcoal from wood, it is stated that the charcoal, particularly if produced from light peat, readily takes fire after it is drawn.

Carbonization by super-heated steam.—Mr. Vignoles, the well-known civil engineer, obtained a patent in 1849 for charring peat by steam super-heated to about the melting point of tin, or even lead.[2] Peat in the state of pulp "is thrown in mass into a cylindrical drum-shaped vessel, divided, if necessary, into compartments, which is caused to revolve with great rapidity upon its axis; the velocity requisite being such as shall drive off the water or other fluid from the solid parts of the peat or turf by centrifugal force." The axis of this cylindrical vessel should be placed vertically, and the cylinder should be from 6 to 10 feet in diameter, and from 1½ to 2½ feet in depth. The external surface of the cylinder is composed of fine wire-gauze, or of perforated sheet-metal, of which the apertures should be of such a size as not to permit the particles of peat to pass through in any considerable degree, but should permit the water to be expelled through them. When the peat, as obtained from the bog, is not sufficiently pulpy, but "in a more consistent or fibrous condition," it may be readily reduced to the "state of a nearly homogeneous mud by the operation of edge-stones or of a pug-mill." As soon as the process for expelling the water has dried the peat into a coherent, consistent mass, it is removed and moulded into blocks. These blocks are put into large cylindrical iron vessels, into which steam at from 45 to 60 lbs. pressure per square inch is admitted, after having been super-heated by traversing iron tubes heated to bright redness. Mr. Vignoles states that he has proved the practicability of the process on the large scale, at an expense of some thousands of pounds; and he has given numerous elaborate calculations of its cost. The charcoal or "coke" was considered to be equal to gas-coke, and the total cost in Ireland of peat charcoal made by this process was estimated at 8*s.* 4*d.* per ton, exclusive of any

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[1] Vogel, op. cit. p. 117.

[2] A.D. Sept. 10, 1849. On the 19th June, 1848, Violette presented a memoir to the French Academy of Sciences on the carbonization of wood by super-heated steam. Vid. Ann. de Chim. 3. s. 23, p. 475.

profit and of payment for patent rights. Mr. Vignoles indulged in sanguine anticipations respecting the effect of his invention upon Ireland. He thus writes:—"This new method of obtaining a coke (which is peculiarly, perhaps absolutely, free from sulphur), when made from the most compact turf, may be looked forward to for restoring the trade of making iron in several parts of Ireland, for the superior quality of the metal would command the English market, and *enable it to compete with the best iron from Sweden.*" The italics are mine. I am not aware that Ireland possesses iron-ores which, in respect of quality and abundance, are to be compared with those of Sweden; and I fear that many years will elapse before the restoration of the Irish iron trade occurs. Mr. Vignoles' process of manufacturing peat charcoal has never, I believe, been adopted either in Ireland or elsewhere. Sir Robert Kane informs me (July, 1861) that the present cost in Ireland of the peat necessary to produce 1 ton of charcoal would exceed by 3*s.* 8*d.* the sum stated in Mr. Vignoles' estimate as the total cost of that amount of charcoal; the price of peat being now about 4 shillings per ton, and 3 tons being necessary to furnish 1 ton of charcoal.

COKE.

History.—The date of the first application of coke as a fuel does not appear to have been ascertained. When charcoal became dear,—especially on account of the increasing consumption of it in iron-works[3]—and pit-coal was coming into general use, attempts would naturally be made to extract from the latter a substance which might be employed with advantage as a substitute for the former; and, obviously, the first experiment would be to subject coal to a process similar to that of charcoal-burning. Coke would thus be produced, and would soon be found to be valuable as a fuel for various purposes.

Until comparatively recent times, coke was always made by burning coal in piles or open fires; and even at the present day coking in this manner is still extensively practised. It is stated that in March, 1651, Jeremy Buck, by a special Act of Parliament, obtained a patent for making iron with stone coal, pit coal, or sea coal *without charking.*[4] Hence it may be inferred that the process of coking was known and practised before that date. The verb "chark" means "to burn to a black cinder;" whereas the meaning of "char" is defined to be "to burn wood to a black cinder."[5]

In Plot's 'History of Staffordshire,' published in 1686, it is recorded

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[3] "The yron Mills are excellent for that;
I have a patent draune to that effect;
If they goe up, downe goes the goodly trees.
I'le make them search the earth to find new fire." — *The Costlie Whore.* London, 1633, B. 4.

[4] Abridgments of the Specifications relating to the Manufacture of Iron and Steel, 1857, p. 3.

[5] Johnson's Dictionary, 9th ed. Longman and Co. London, 1805.

that coal was charred in exactly the same manner as wood; and that the coal thus prepared was called "coak," which was capable of producing almost as strong a heat as charcoal itself. It was used in drying malt, and could generally be employed as a substitute for charcoal, except "for *melting*, *fineing*, and *refining* of iron, which," says Plot, "it cannot be brought to doe, though attempted by the most skillfull and curious *artists*."[6]

Swedenborg, writing in 1734, informs us that in certain districts in England coke was employed in the smelting of iron.[7] Cinders and coke,—or, as it was spelled, coak,—were synonymous. In 1769 Jars announced the fact that coke was made in England, not only in piles, but also in a closed furnace, which, I presume, may be interpreted to mean oven, although he gave no description of its construction.[8] The iron-masters of Liège, a short time afterwards, adopted with success this method of coking. At about the same time, according to Horne, coking in ovens was carried on in the villages round London, the coke being prepared for the use of maltsters and some other purposes. He has given the following description of the process:—"These ovens being from time to time charged with a proper quantity of coals, they set them on fire. Near the front or opening of these ovens the chimneys are placed; at which outlets, when the coals become sufficiently ignited, the flames, which play round the interior parts of the oven, make their exit, carrying along with them a very considerable part of crude sulphur. The workmen employed at these ovens, when they imagine the coals are sufficiently burnt, draw them out with an iron raker upon the ground before the oven, where they endeavour to stifle the yet remaining part of the sulphur by quenching them with a deluge of water. Thus they go on charging, discharging, and suffocating till they have completed their intended quantity."[9]

An experimental coke-oven, on a plan proposed by Horne, was erected in Staffordshire, and, it is stated, with a successful result. The details of the plan are not given. It appears, however, that the oven consisted of a closed arched chamber, and that on trial it was found to be desirable to leave some outlet "in the top of the crown" for the escape of vapour, in order to prevent the blowing-up of the furnace, or oven. In 1781, according to Bishop Watson, the application of coke to the smelting of iron seems to have become general in this country.[1] The Bishop also informs us that coke-ovens were in use at the same period at Newcastle-on-Tyne and Cambridge.

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[6] The Natural History of Staffordshire. By Robert Plot, LL.D., Keeper of the Ashmolean Museum, and Professor of Chymistry in the University of Oxford. Oxford, 1686, p. 128.

[7] "Interdum vel aliquibus in locis usurpare volunt carbones fossiles, sed qui in cineres aut in *cindres* (cinders), ut vocantur, primum combusti aut calcinati sint." Regnum Subterraneum sive Minerale de Ferro, etc. Dresdæ et Lipsiæ, folio, 1734, p. 156.

[8] Voyages Métallurgiques. Paris, 1774, p. 337.

[9] Essays concerning Iron and Steel. With an Appendix, discovering a more perfect Method of Charring Pit-Coal, so as to render it a proper Succedaneum for Charred Wood-Coal. By Henry Horne. London, 1773, pp. 205-207.

[1] Watson's Chem. Essays, v. 2, p. 344, 4th ed. The preface is dated 1781.

Properties of Coke.—The coke occurring in commerce differs considerably in external characters. Thus, it may be porous and light,—compact and heavy,—soft and tender, or hard and resisting,—black and dull, or light grey and of a bright, almost metallic lustre,—and occasionally iridescent. It also varies much in degree of combustibility. Coke which is good for one purpose may be bad for another. Hence, irrespective of the particular application for which coke is intended, it is not possible to present an assemblage of qualities which may be said to characterize all good coke. In certain metallurgical operations coke is required to support considerable pressure without crumbling, while in others it is scarcely exposed to greater pressure than coal in an ordinary fire-place. It is also necessary that coke should be more or less easily combustible, according to circumstances. The quality of coke depends not merely upon the nature of the coal from which it is derived, but also upon the manner in which the process of coking is conducted.

Composition of Coke.—Coke which has been well prepared consists essentially of carbon and the fixed inorganic matter of the coal from which it has been obtained. It retains, however, hydrogen, nitrogen, and oxygen in small proportion, in proof of which the following analyses of railway coke by M. de Marsilly may be cited:—

	1.	2.	1. Exclusive of Ash.	2. Exclusive of Ash.
Carbon	91·30	91·59	97·33	97·33
Hydrogen	0·33	0·47	0·35	0·50
Nitrogen and oxygen	2·17	2·05	2·32	2·17
Ash	6·20	5·89	..	..

The coke was made from the caking coal of the Mons basin, in ovens with heated bottoms, the process of coking continuing during forty-eight hours. The specimens analysed were previously dried at 200° C.

Presence of Water in Coke.—The coke of commerce always contains water, of which the quantity in some cases may be very considerable. When the extinction is properly conducted, coke, according to M. de Marsilly, should not retain more than from 2 to 3 per cent. of water, though occasionally it has been found to retain as much as 5 or 6 per cent. When the coke-burners are paid according to the weight of coke produced, or when the coke is purchased by weight, it is important that the proportion of water should be determined. M. de Marsilly ascertained that perfectly dry coke will not absorb more than from 1 to 2·5 per cent. of water by exposure to an atmosphere saturated with moisture at ordinary temperatures. We are indebted to the same author for the following facts: Perfectly dry coke may, by immersion in water during twenty-four hours, absorb as much as 51 per cent. of its weight. In eleven experiments this was the greatest amount of absorption, and the least was 12·5 per cent.; the average being 36·25 per cent. Before immersion, the coke was dried between 100° and 200° C., and weighed; and after its immersion it was taken out of the water, drained, and weighed again. The greater part of the water thus

absorbed is soon evaporated when the coke is exposed to the open air. It is scarcely necessary to remark that when coke is required to produce its maximum calorific effect, it should be as dry as possible.

General considerations on the Preparation of Coke.—When a mass of coal is subjected to destructive distillation, as in a common gas-retort, it is obvious that the coal which first comes in contact with the red-hot surface of the retort must be exposed to the highest degree of heat, and that for some time afterwards the temperature will gradually diminish through the mass in proportion to the distance from that surface; and when a large quantity of coal, say several tons, is thus heated in one chamber, a considerable time must necessarily elapse before the whole mass can be heated to the same degree. Hence, until uniformity of temperature is attained, the destructive distillation of the coal in different parts will be taking place at different degrees of heat; but the nature of the products varies with the temperature at which the distillation is effected. At a low temperature substances rich in carbon and hydrogen are generated, which at a higher temperature are decomposed with the *deposition of carbon*. In coking, therefore, as the object is to retain the greatest amount of carbon possible in the coke, it might be inferred that the temperature at which the process is conducted would exert a decided effect on the yield of coke. In illustration of the fact of the deposition of carbon in the manner above stated may be adduced the well-known solid deposit of carbon which accumulates on the internal surface of gas-retorts. When olefiant gas, one of the products of the dry distillation of coal, is passed through a red-hot porcelain tube, it is decomposed with the separation of carbon and the formation chiefly of marsh gas.[2]

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[2] I am indebted to my colleague, Dr. Hofmann, for the following complete list of the compounds generated by the destructive distillation of coal:—

Carbonic oxide	C^2O^2
Carbonic acid	C^2O^4
Sulphurous acid	S^2O^4
Hydrosulphuric acid	H^2S^2
Bisulphide of carbon	C^2S^4
Hydrocyanic acid	HC^2N
Hydrosulphocyanic acid	HC^2NS^2

Hydrocarbons.

Marsh gas	C^2H^4
Acetylene	C^4H^2
Olefiant gas	C^4H^4
Propylene (?)	C^6H^6
Caproylene	$C^{12}H^{12}$
Oenanthylene	$C^{14}H^{14}$
Paraffin	C_nH_n (?)

Propyl	$C^{12}H^{14}$
Butyl	$C^{16}H^{18}$
Amyl	$C^{20}H^{22}$
Caproyl	$C^{24}H^{26}$

Benzol, Parabenzol	$C^{12}H^6$
Soluol	$C^{14}H^8$
Xylol	$C^{16}H^{10}$
Cumol	$C^{18}H^{12}$
Cymol	$C^{20}H^{14}$

Naphthalin	$C^{20}H^8$
Paranaphthalin	$C^{30}H^{12}$

Chrysen	$C^{12}H^4$ (?)
Pyren	$C^{30}H^{12}$ (?)
Eupion	(?)

Acid Compounds.

Acetic acid	$C^4H^4O^4$
Phenylic acid or phenylic alcohol	$C^{12}H^6O^2$
Cresylic acid or cresylic alcohol	$C^{14}H^8O^2$
Phlorylic acid or phlorylic alcohol	$C^{16}H^{10}O^2$

Rosolic acid	$C^{46}H^{22}O^6$ (?)
Brunolic acid	(?)

Other products of the distillation of coal are similarly decomposed by exposure to a high temperature. In this manner the formation of the deposit in question, or gas-retort carbon, as it is termed, admits of easy explanation. Now, in the preparation of coke, carbon may be deposited upon the coke in precisely the same manner. Let us suppose coal piled to the thickness of two or three feet in a fire-brick chamber, entirely closed, with the exception of a hole in the top to act as a chimney, and a few small openings through which air from without may enter, *above* the surface of the coal; and let us further suppose that the whole of the upper part of the coal is burning actively, air to sustain combustion entering through the small openings, and the products of combustion escaping through the hole in the top. The oven above the coal will speedily be heated to redness, and heat will be propagated downwards through the coal, of which every portion will be successively subjected to destructive distillation. The volatile products from below will ascend; but in traversing the red-hot stratum of coked coal above, they will partially suffer decomposition: the coked coal will be coated with a deposit of lustrous carbon, while the more or less decarbonized residual gases will take fire as they escape from the incandescent mass. The coke which is formed above will continue to be enveloped in an ascending current of volatile products, and will be thereby protected from the action of the air, and so from burning to waste.

Occasionally hair-like threads are observed on pieces of coke. They are solid, and under the microscope present somewhat of the appearance of a string of beads which have been soldered together. They consist of carbon, which seems to have been deposited on bubbles of gas. One bubble being produced, a second is then formed in connection with the first, and so in succession until the completion of a continuous tube, constricted at the junction of every two bubbles. Gas would continue to flow through this tube, depositing carbon in its course on the *inner* surface, until at length the tube is converted into a nearly solid fibre. Such appears to me to be the mode of formation of this curious hair-like matter, though I am by no means certain of the correctness of this view.

When caking coals are thus heated, they first agglutinate into one mass, which, as the process proceeds, becomes fissured from top to bottom so as to form a series of columnar pieces, resembling the columnar structure which is induced in sandstone by the long-con-

Basic Compounds.	
Ammonia	H^3N
Aniline	$C^{12}H^7N$
Pyridine	$C^{10}H^5N$
Picoline	$C^{12}H^7N$
Lutidine	$C^{14}H^9N$
Collidine	$C^{16}H^{11}N$
Parvoline	$C^{18}H^{13}N$
Chinoleine / Leucoline	$C^{18}H^7N$
Lepidine	$C^{20}H^9N$
Cryptidine	$C^{22}H^{11}N$
Pyrrol	C^8H^5N (?)
Hydrogen	H

The equivalent numbers of CO, CO^2, etc., are given as C^2O^2, C^2O^4, etc., the numbers now adopted by Dr. Hofmann.

tinued action of a high temperature, or the structure which starch acquires by desiccation. To this state of aggregation the term crystallization is frequently, though very erroneously, applied.

The quality of coke is much affected by the degree of heat and duration of the coking process. It may be stated as a general rule that the higher the temperature, and the longer the exposure to that temperature, the harder, more dense, and less easily combustible will be the coke. M. de Marsilly tried the effect of coking during 96 and 120 hours, but found that no advantage was derived by prolonging the process beyond 48 hours.

Coking in Piles.—The terms coke-hearth and coke-fires are employed synonymously with piles. The piles are either circular or in the form of heaps having a long narrow rectangular base. The ground on which they rest should be flat, dry, and solid; and a plentiful supply of water should be at hand.

Circular Piles.—They vary considerably in size according to circumstances and the caprice of the coke-burner. The annexed woodcut represents a pile of this description which I saw at the Russell's Hall Furnaces, near Dudley. The diameter at the base was 30 feet. The bed was of earth, not brick. In the centre is a chimney, built of bricks without mortar; it is shown in elevation at *a*, and in plan at *b*.

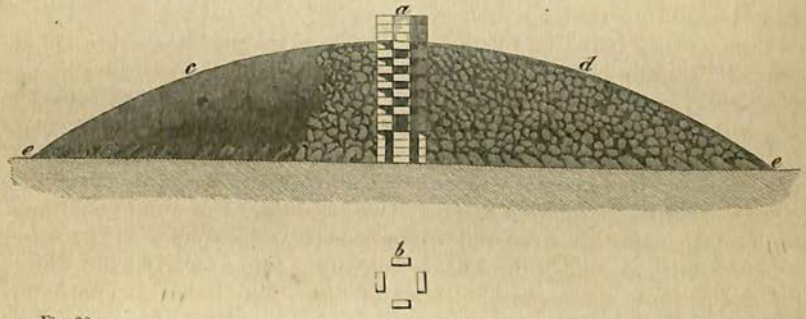

Fig. 20.

The heat of the pile is sufficient to vitrify the surface of the bricks, and so firmly to unite them together. Four bricks are first laid as in *b*; upon each brick three others are placed, and thus four pillars of four bricks each are formed. Across the ends of these pillars two courses of bricks are laid, and then the chimney is continued upwards by placing the bricks circularly, so as to leave regular spaces between their ends all round, as shown in the woodcut. The upper part of the chimney is built without spaces. A large flat brick may when necessary be placed on the top to act as a damper; or a suitable iron damper may be provided, as shown in the annexed woodcut, fig. 21. It is a cylinder of cast-iron, about 14 in. high and 10½ in. in internal diameter; at the bottom is a flange, which rests on the top of the brick chimney.

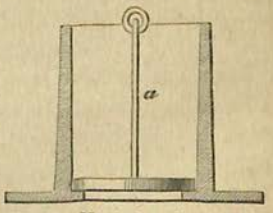

Fig. 21. Vertical section through the centre.

The diameter of the opening at the bottom is 8 in. When necessary, the damper, *q*, consisting of a disc of iron, provided with an upright handle, is dropped in. The damper is covered over with sand when it is desired to close the chimney perfectly. The coal employed was the pot-caking thick or ten-yard coal. The large coal is stacked round and inclining against the chimney, and then follow the lumps (smaller coal); when the stacking of the coal is completed, the whole surface of the pile is covered with a layer of coke-dust from previous burnings, *except round the bottom of the pile, e e, to the height of about a foot.* The height of the pile from the centre to the highest part near the chimney was five feet. The dark shaded part, *c*, on the left of the chimney is a view in elevation of that part, the rest of the pile on the right being a vertical section through the centre of the bed, with the exception of the chimney, which, as has been previously stated, is seen in elevation. In some piles the chimney was larger, and rested on six pillars of bricks instead of four. The diameter at the base of a chimney of this kind was 3 ft. 3 in. outside measure; and circular bricks were employed. In the pile described, about 20 tons of coal (1 ton = 2640 lbs.) were stacked. Ignition is effected by putting live coals on one side of the chimney near the top. Combustion is thus conducted downwards through every part of the mass. Thick smoke speedily appears, and flame issues from the chimney and various parts of the surface. The progress of the coking is carefully watched; where the combustion appears too vigorous, the coker damps it by applying coke-dust. After a time beautiful blue flames of carbonic oxide appear here and there over the surface. When coal smoke ceases to escape, and the process of burning is completed, which will occur in about 5 or 6 days, wet coke-dust is plastered over every part of the surface of the pile by means of a spade, and the chimney is perfectly closed. In windy weather much attention is necessary on the part of the coke-burner to prevent as far as practicable the waste which is liable to occur from the increased combustion of the part exposed to the wind. Numerous precautions are necessary to ensure a successful result, but these can only be learnt by experience. Simple as the process may appear, yet the men who conduct it differ much in their degree of skill. On about the tenth day after lighting the coke may be drawn. Before drawing the pile is watered; that is, water is thrown upon it. The yield from such a pile was stated to be 3¼ barrows to the ton of coal (2640 lbs.) or 13 cwt., that is 65 per cent. of the coal. This information was not based on exact data, and I should be inclined to consider the amount as too great. A considerable quantity is burned to waste in this method of coking, as may be inferred from the layer of ashes covering the entire surface of the pile at the conclusion of the process.

At the Coalbrook Vale Iron-Works, South Wales, I observed coking in circular piles about 18 ft. in diameter at the base and 6 ft. high in the centre. Mr. James, the furnace manager, informed me that the pile was lighted at these works by putting live coals down the chimney, and that the coal round the bottom became first ignited.

From thence the fire creeps towards the outside of the pile round the base, and extends upwards; and in proportion as it rises, the surface of the pile underneath is damped in the usual way. A column of flame 2 ft. high may continue to issue from the chimney during some time after lighting. The chimney is left open till the fire nearly reaches the top, when it is covered with an iron plate. In Mushet's description of this process,[3] it is stated that brick flues, or channels formed by pieces of coal, are laid to communicate with the lower tier of holes in the chimney, so as to conduct the air through the interior of the mass. In other respects the description is similar to that last given. Mushet, however, observes that as the fire proceeds upwards the ignited surface of the exposed coal (which forms a zone never more than 4 or 5 inches broad) is from time to time covered with coke-dust and a new surface exposed, the dust crumbling above and protecting the ignited surface of the recently formed coke below. In this way the fire in 2 or 3 days reaches the upper surface, when the flame in the chimney becomes less, until it dies away altogether. Mushet further remarks that this process may be modified so as to yield coke of different qualities from the same kind of coal. When the opening round the bottom of the pile is much diminished the process is retarded, and the fire requires a longer time to reach the outer surface. The yield thus obtained is said to be greater than when the coking takes place more rapidly; the coke is darker, less combustible, has a higher specific gravity, and is little changed in form (from the original coal?). On the other hand, when the pile is left open round the base to the height of a foot, combustion proceeds more rapidly on account of the freer access of air; a higher temperature is produced; the coke is honeycombed; is more grey in colour; has a lower specific gravity; is more combustible; and less in quantity.

According to Mushet this system of coking under wetted dust was introduced at the Muirkirk and Clyde Iron-Works about the year 1801, and in a few years became general at the Scotch furnaces. In 1805 it was introduced into Derbyshire, and subsequently into Staffordshire, Yorkshire, and Shropshire. He further states that it had been attempted at Merthyr, but without success, as the coal passed "almost unchanged in form into a ponderous coke resembling anthracite;" and at other works in South Wales in which a caking coal was employed, it was tried and abandoned in consequence of the slow combustion occasioned by the welding of the coal, and the rents and cracks caused upon the surface of the pile by the great enlargement of its volume.[4] Now it has been shown that in Staffordshire coking in piles was commonly practised long anterior to 1805; but Mushet probably means to intimate that a covering of "wetted dust" had not been previously applied. In times anterior to that date the pile seems to have been constructed exactly like a charcoal pile, and to have been covered with straw, leaves, and soil in succession.[5]

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[3] Papers on Iron and Steel, 1840, p. 304.
[4] Op. cit. p. 304.
[5] Traité Méthodique de la Fabrication du Coke, etc. Par M. Pelouze, père. Paris, 1842, p. 9.

Coking in long Piles or Ridges.—These piles, which are technically termed "pits," may be extended to any length, and may be conveniently arranged in parallel rows. At the Coalbrook Vale Iron-Works, I measured one, of which the transverse section at the base was 12 ft., and the height in the centre 3 ft. 6 in. A pile of these dimensions will contain from 2 tons 10 cwt. to 3 tons per linear yard. Mr. Levick informs me that they vary from 4 to 5 ft. in height in the centre, and from 9 to 12 ft. in width at the base. There are no chimneys as in the circular piles. A layer of small coal, from 16 to 12 in. thick, is left at the bottom; and upon this the large coal is stacked, inclining towards the middle of the ridge, and in such a manner as to leave air passages all through the inside of the pit; the outside is covered with a layer of small coal. The pile is lighted at short intervals along the top, and the combustion is conducted downwards. As the flame ascends up the outsides of the pile, the coker continues to damp them with wet coke-dust until the coal is completely coked throughout; when this occurs the pile is well plastered over with wet coke-dust, and then left to itself. Before the fire is quite extinguished the pile is watered and the coke drawn as required.

COKING IN LARGE OPEN RECTANGULAR KILNS.—A description of this method, as practised at Gleiwitz, in Upper Silesia, was published in 1851 by Brand,[6] who states that it had been previously in operation in the principality of Schaumburg Lippe, where a pure but very tender and strongly caking coal is raised. According to Brand, who is manager of the iron-works at Gleiwitz, and who writes from personal experience on the subject, the advantages of this method are, that it requires only a very moderate outlay, and produces a dense coke of excellent quality.

The kiln consists of two parallel walls of brick, *a*, *a*, fig. 23, and a flat bed, *b*, of bricks set edgewise, underneath which is a stratum of a glassy blast-furnace slag broken small, so that proper drainage may be secured. Fire-bricks are only used to form the bed and the inner surface of the walls; the walls are five feet high, eight feet apart in the clear, and from 44 to 60 feet long (Prussian measure). In each wall is a series of transverse openings, *c*, *c*, &c., at a distance of two feet from each other, and at the same height above the ground, so that the openings in one wall are respectively opposite to those in the other. From each of these openings, *c*, rises a vertical chimney, *d*. The charging of the kiln is effected as follows: One of the end openings, *e*, *e*, is bricked up, and through the opposite one coal slack is wheeled in, spread over the bottom, watered, and stamped down so as to form a solid stratum nine inches thick, or as high as the lower edges of the openings, *c*, *c*, &c.; indeed, the height may be made two feet with advantage, if the coal be suitable. Pieces of wood, six inches in diameter at one end, and four at the other, and in length equal to the width of the kiln, are then passed through the openings in one wall so that their opposite ends may respectively lie in the

[6] Berg. u. Hüttenmän. Zeitung, April 2, 1851, V. 10, p. 217.

corresponding openings in the other wall. Wetted coal slack is spread over the pieces of wood, and stamped carefully down. The kiln is then filled up with slack, which at every six inches of additional height should be watered and stamped down. Brand well remarks that the mode of filling just described is very hard work when the kiln exceeds 40 feet in length. After the filling is completed, the top of the coal is covered with a layer, two or three inches thick, of coal-dust; or, failing this, of loam. The end opening through which the kiln has been charged is at last bricked up. The pieces of wood are now carefully drawn out, and thus a series of channels are formed in the coal, upon the maintenance of which the success of the process essentially depends. Should an injury occur to any of the channels at the commencement, it can hardly be repaired afterwards. Before lighting the kiln, all the chimneys on one side are stopped by placing a brick on the top of each (see fig. 25, *d*), those on the opposite side being left open; while on this side the openings or draught holes are stopped by bricks, fig. 25, *c'*, the holes on the opposite side being left open, as in *c*. The kiln is now lighted by means of sticks of easily inflammable wood introduced into all the openings, *c*, on the left. A current of air is established through the transverse channels

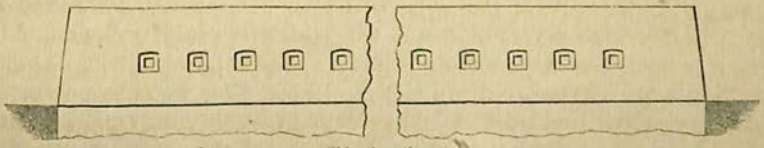

Fig. 22. Side elevation.

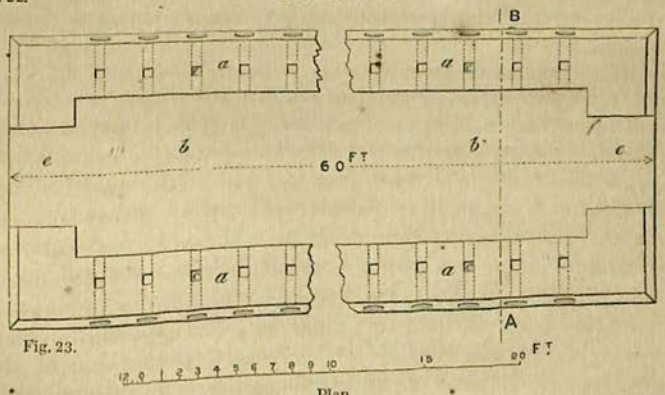

Fig. 23.

Plan.

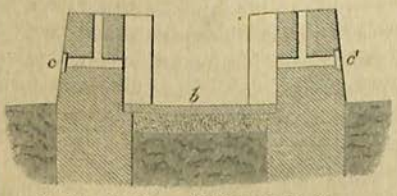

Fig. 24. Section on the line A B, fig. 23.

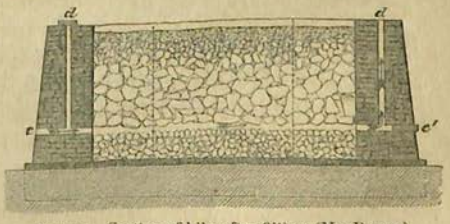

Fig. 25. Section of kiln after filling (Mr. Rogers).

in the coal, in the direction indicated by the arrows. After the lapse of six or eight hours the fire will have reached the opposite ends of these channels, when the chimneys on the left, *d*, and the draught holes on the right, *c'*, must be opened, and the chimneys on the right, *d'*, and the draught holes on the left, *c*, must be closed. This, however, should only be done when the fire has regularly spread through the entire extent of the channels. Special care in this respect at the commencement will prevent further trouble afterwards. According as the weather is stormy or settled, the direction of the currents of air through the kiln may be changed from every two to four hours. Should the coking be found to proceed irregularly, it may be necessary to keep open some of the chimneys on one side longer than others, and, consequently, not at once to change the direction of all the currents. Irregularity in the coking may depend either upon the quality of the coal or negligence in piling it in the kiln; and in either case the yield may be diminished.

In the management of the process the work of the coke-burner is reduced to keeping open the transverse channels in the coal by raking out any pieces of coal which may fall into them and obstruct the passage of the air, and in preventing them from sintering together. For this purpose he uses a slender iron rod, somewhat bent at one end. The re-opening of a channel which has once become stopped is attended with much difficulty, and is generally impracticable; and if several neighbouring channels are closed, the process is thereby much impeded. In windy weather the draught of air through the kiln must be carefully regulated by closing, in a greater or less degree, the chimneys. Any cracks which may occur during the process in the covering on the top of the coal must be well stopped, in order to prevent the ascent of currents through them. The proper regulation of the draughts through the kiln has an important influence upon the quality as well as the yield of coke.

In about eight days the process will be completed, as may be known by the escape of white flame from the chimneys and the hardness which is perceived on plunging an iron rod through the cover on the top. All the openings must now be closed, and in the course of two days afterwards the fire will be gradually extinguished. One of the end walls is taken down and the coke removed. The coke at the height of the channels will be separated into two distinct layers; that in the upper layer especially is remarkably beautiful (*sic*), dense, hard, and when carefully withdrawn is frequently in pieces 3 feet long and 1 foot in diameter. The yield per 7·768 cubic feet (English) of coal ranged from 241·25 to 261·87 lbs. (avoirdupois). The loss in weight is 20 per cent. of the coal, an amount which, according to the quality of the coal, is often much reduced. For the measure of coke above mentioned the workmen received just over 1¾*d.* The coke produced by this method is stated to have yielded most excellent results in the cupola, 1·36 cubic feet (English) being used to melt from 283 to 510 lbs. (avoirdupois) of pig-iron, according as it is intended to be run into thin vessels (Potterie) or heavy castings.

In the vicinity of Sarrebrück experiments have been made with kilns 10 feet high, having in the middle of each side a second row of draught holes; but the result was unfavourable, and the kilns were abandoned.

Several years after the publication of the preceding description,[7] the same process was patented in England. On the 28th January, 1857, my friend Mr. Rogers, of Abercarn, communicated to the Institution of Mechanical Engineers in Birmingham a paper on the manufacture of charcoal and coke, in which he introduced to their notice the process in question. In that paper the following passage occurs:[8] "A short time ago a plan was mentioned to the writer as having been used in Westphalia, by which wood was charred in small kilns; as the form of kiln described was quite new to him, it led him to some reflection as to the principles on which it acted, which were found to be so simple and effective, that he determined to apply them on a large scale for coking coal. The result has been that in the course of a few months the original idea has been so satisfactorily matured and developed, that instead of coking six tons of coal in an oven costing 80*l.*, 150 tons of coal are now being coked at once in a kiln costing less than the former single oven." The description and drawings of the kiln contained in the paper prove that in every essential point it is identical with that which I have just described. Mr. Rogers is mistaken in supposing that coal had not previously been coked in such kilns.

The theory of coking by this method is perfectly intelligible. The coal surrounding the transverse channels is ignited, and through these currents of air are established. Heat is thus developed partly by the combustion of the coal in the vicinity of the channels, and partly by that of the volatile products arising from the destructive distillation of the coal. The coking will, therefore, proceed simultaneously upwards and downwards. No currents, as has already been stated, can ascend through the coal above the channels, if the kiln be properly attended to. The air which sustains combustion can only enter the kiln through the lateral draught holes; and, obviously, none can descend from above. At the conclusion of the process an accumulation of tarry matter always occurs immediately under the coal at the top of the kiln, which would further tend to prevent the descent of air from above as well as the ascent of currents from below; and it is there that the most solid coke is produced.

In South Wales, and I believe also in other districts, kilns of this kind have been erected of not less than 15 feet in width from wall to wall, measured within. The transverse channels may be made by suitably piling lumps of coal. When the coal is of different sizes, it is advantageous, according to Mr. Rogers, to let the size of the pieces diminish towards the top of the mass. In these larger kilns the mass

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[7] It was also published in England in 1855. Vide Chemical Technology, Baillière, London, v. 1, p. 117.

[8] Proceedings of the Institute of Mechanical Engineers, 1857, p. 31.

becomes well ignited in from twenty-four to thirty-six hours. During the process the workman walks on the top of the coal; and from time to time at different parts of the surface he inserts an iron bar, which is easily pushed down until it reaches the mass of coke. In this way the height to which the coking process has reached is satisfactorily ascertained: if he finds it to have progressed higher at one part than another, he closes the chimney communicating with that part, and so retards the process there. When the mass has been coked up to the top, which takes place in about seven days, it is quenched with water, and the coke withdrawn in the manner already described.[9]

"The new kilns," writes Mr. Rogers, "have proved entirely successful; they are already in use at some of the largest iron-works in the kingdom, and are being erected at a number of other works. The great saving in the first cost of oven, economy in working and maintenance, increased yield, and improved quality of coke, will probably soon cause this mode of coking to supersede the others now in use. The kilns are most advantageously made about 14 feet in width, 90 feet in length, and 7 feet 6 inches in height: this size of kiln contains about 150 tons of coal."

Mr. Rogers asserts that an outlay of only 4*l.* is required to produce one ton of coke per day from the Welsh coals, and that the cost of working does not exceed 6*d.* per ton. In some places the coal has been actually tipped into the kiln from the colliery waggons, and the coke waggons were afterwards run into the kiln to be loaded direct from the mass of coke produced, thus reducing the labour to a minimum. The kilns need only be built of rough rubble work with a plain lining of fire-brick and without any iron work, so that the expense of repairs amounts only to a small sum. This exactly accords with Brand's experience of the German kilns.

When interrogated at the meeting before which the paper was read as to the yield of coke by this method, Mr. Rogers replied that 18 cwt. per ton of coal (Welsh) had been obtained, an amount nearly equal to that of the carbon which existed in the original coal. It is hardly necessary to observe that this statement *must* be erroneous. It does not appear that the proportion of water retained by the coke after quenching had been determined; and if this had been done, the result would probably have been widely different. Mr. Riley informs me that he found as much as 22 per cent. of water in coke prepared at the Dowlais Iron-Works by the method in question.

In 1859 I visited several of the large iron-works in South Wales where these kilns had been tried, and I inquired particularly concerning the results. Opinions on this subject were certainly not concordant. At the Dowlais Iron-Works they have been erected, and after repeated trials abandoned.

The Ebbw Vale Iron Company has also made trial of them, and my friend Mr. Adams, the manager, informs me that they appear to be adapted to one kind of coal, but that for their usual good coal they are

[9] Vide paper above referred to, p. 32, from which I extract these details.

wasteful and expensive; much of the large coal which is used to form the transverse channels is burned away, and as he quaintly observed, "you might hunt badgers through the coke." At Pontypool Iron-Works I inspected one of these kilns from which the coke had been partially drawn, and I remarked that a good deal of the coal opposite the draught holes appeared to have burned away: some of these kilns were much higher than I had seen elsewhere. Experiments have been made at these works with kilns having double rows of draught holes on each side; but I am informed the result was not satisfactory.

Coke-Ovens.—In its simplest form a coke-oven is a chamber of fire-brick or some other refractory material, having an arched roof in which is a hole and an entrance below. Many years ago Parkes described ovens of this kind, which were in use at the Duke of Norfolk's Colliery near Sheffield.[1] Each oven was a circular building 10 ft. in diameter within, having a floor laid with common bricks set edgewise. The wall of the oven rose perpendicularly 19 inches above the floor, and was covered with a brick arch rising 3 ft. 5 in. in the centre and forming a cone, which measured within was 10 ft. at the base and 2 ft. high at the apex. The opening at the top acted as a chimney during the process of coking, and through it the coal was introduced. The entire height of the oven from the floor to the top of the arch, outside measure, was 5 ft.; the surrounding wall, 18 in. in thickness, was built with good bricks closely laid, so that no air might get in through any part of the work. The floor was raised 3 ft. above the ground for the convenience of placing a low carriage under the doorway, to receive the coke as it was raked from the oven. The oven was enclosed up to the top in a square, formed by four vertical walls, 20 in. in thickness, and built of rough unhewn stone. The four corners between the circular oven and the surrounding walls were filled with soil or rubbish, which was well rammed to give greater firmness to the work, and the more effectually to exclude the air.

Parkes has given the following excellent description of the mode of conducting the process, which cannot well be improved, and which is applicable to coking in ovens as practised at the present time. When once the ovens are heated, the work goes on night and day without interruption, and without any further expense of fuel. Small refuse coal is thrown in through the hole in the top, sufficient to fill the oven up to the springing of the arch; it is then levelled with an iron rake, and the doorway built up with loose bricks. The heat which the oven acquired in the former operation is always sufficient of itself to light up the new charge, the combustion being sustained by the entrance of atmospheric air through the joints of the loose bricks in the doorway. In two or three hours it is necessary to check the influx of atmospheric air by plastering up the doorway with a mixture of wet soil and sand, except the *top* row of bricks, which is left unplastered all night. Next

[1] Chemical Catechism, 12th ed., 1826, p. 453.

morning, after the charge has been in the oven twenty-four hours, this row is also completely closed; but the chimney remains open until the flame is gone, which is generally quite off in twelve hours more; a few loose stones are then laid on the top of the chimney, and closely covered with a thick bed of sand or earth. All connexion with the atmosphere is now cut off, and in this state the whole remains for twelve hours more to complete the operation. The doorway is then opened, and the coke is raked out into wheelbarrows, or low waggons, to be carted away. About two tons of coal are put in for each charge. The coke thus produced is ponderous, extremely hard, of a light grey colour and shining metallic lustre. It is used in those manufactures that require an intense and long-continued heat.

The coal is thus subjected to destructive distillation; the volatile products, as they escape from the surface of the mass, meet with atmospheric air, take fire, and burn, with the evolution of much heat. Combustion is thus sustained along and above the surface of the coal, and the process of coking is gradually propagated from above downwards.

It is evident that the coal underlying the incandescent stratum must be exactly in the condition of coal undergoing distillation in a close vessel; for air is supposed only to enter the oven *above* the level of the coal. A current, therefore, of inflammable gases and vapours will continue to ascend until the lowermost stratum of coal is converted into coke. Hence it might be inferred that the process of coking in ovens would be effected, at least to a considerable extent, by the heat developed by the combustion of the volatile products evolved.

Ovens have been made circular, more or less oval, or rectangular; and in dimensions they have varied considerably. Contrivances have from time to time been adopted with the following objects:—First, to prevent as far as practicable the escape of heat from the oven; secondly, to effect the admission of air so as most completely to burn the volatile matters evolved from the coal; thirdly, to economize the waste heat so as to cause the process of coking to proceed from below upwards as well as from above downwards; and fourthly, to facilitate the removal or *drawing* of the coke from the oven, with the view, not merely of diminishing labour, but also of reducing as much as possible the amount of heat which, in a greater or less degree, must necessarily be lost during this part of the operation.

The first object has been accomplished by making the walls thick, and covering the roof with sand, or some other bad conductor of heat; by building a second arch at some distance over that which forms the roof of the oven proper, and causing the products of combustion to pass between the two arches in their way to the stack; and by constructing in one rectangular pile of building two parallel rows of ovens back to back. The second object has been effected by allowing the air to enter the oven in several places, and accordingly passages have been formed in the brickwork by which air may pass through the sides or back, *above* the surface of the coal; the supply of air through the front being either wholly or partially stopped. The third object has been achieved

by causing the products of the combustion within the oven to circulate through flues immediately under the bottom, and sometimes also round or down the sides. The fourth object has been attained by building the oven rectangular below the arched roof, and a little wider in front than at the back; then on the floor at the back is placed an instrument called a drag, which consists of a strong piece of flat iron, having attached to it at right angles a rod of iron sufficiently long to protrude beyond the front of the oven. This drag is left in the oven during the process of coking, after the completion of which the whole mass of coke may be drawn out at once by means of a windlass in front, with which the protruding end of the drag has been connected. In some ovens a small gutter is made from front to back in the floor of the oven; and only the transverse piece of the drag is left in the oven. The gutter is covered over with little pieces of bar-iron preparatory to charging it with coal, in order that it may not become obstructed. Just before the coke is drawn, a long rod of iron, called a *needle*, is pushed along this gutter, and by a simple contrivance catches hold firmly of the centre of the transverse piece, after which the operation may be proceeded with in the manner described. By this arrangement the destruction of iron which occurs when the entire drag remains in the oven is considerably diminished.

As soon as the coke is drawn, it is extinguished with water, of which a copious supply should be always at hand. The mouth of the oven may be stopped either by building it up with bricks, or by a door consisting of a framework of cast-iron, in which fire-bricks are set. The door may be made in two parts, and hinged like an ordinary folding-door, or it may consist only of one piece, and may be raised or lowered by means of a chain passing over a pulley above, and having a counterpoise weight at the end. The charging is generally effected through a hole in the roof, to which the coal is conveyed on a railway along the top of a pile of ovens. When the coke is not drawn out in mass, it must be removed in pieces, which will obviously occasion a greater expenditure of time and labour, and the oven will in consequence lose much heat, especially if water be injected into it to extinguish the coke. Instead of *drawing* out the coke at the front, it may be *pushed* out from the back by a suitable apparatus, capable of being moved along a railway from one oven to the other in succession.[2] This method of drawing is employed at Cyfartha and at Beaufort.

I have selected for special description the following series of ovens, as sufficient to illustrate the essential modifications which have been proposed and adopted.

Cox's Coke-oven.—This oven was patented in 1840.[3] I am indebted to the Ebbw Vale Iron Company for the drawings from which the annexed engravings were made. The oven consists essentially of a nearly-rectangular chamber of fire-brick, arched over from side to side,

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[2] Engravings of such apparatus are given by Dieudonne in his Mémoire sur la Fabrication du Coke à Forbach et Hirschbach. Ann. d. Mines, 5. s. 15, p. 489. 1859.

[3] Vide published Specifications, No. 8709, A.D. 1840.

and open in front. The bottom is flat, and inclines slightly downwards and forwards: see fig. 27 ε. The width between the side walls increases gradually, but only in a small degree from back to front, as shown by the dotted lines, fig. 28. At a distance above the arch forming the roof is a second arch, fig. 26 β and fig. 27 ε. The side walls and the front wall above the arched mouth are carried up to a considerable

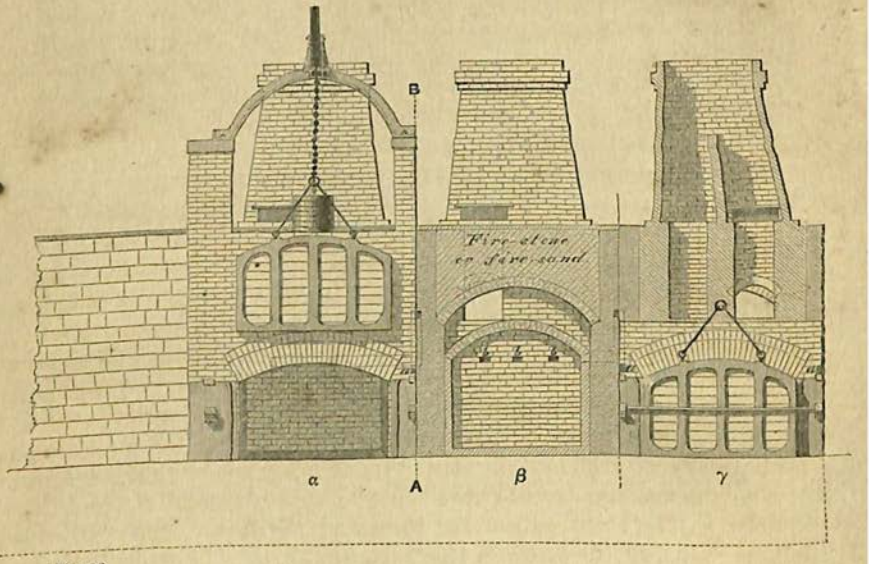

Fig. 26.
α Front elevation. β Section on the line G H, fig. 28. γ Section of the stack on the line I J, fig. 28, above the top of the lower arch.

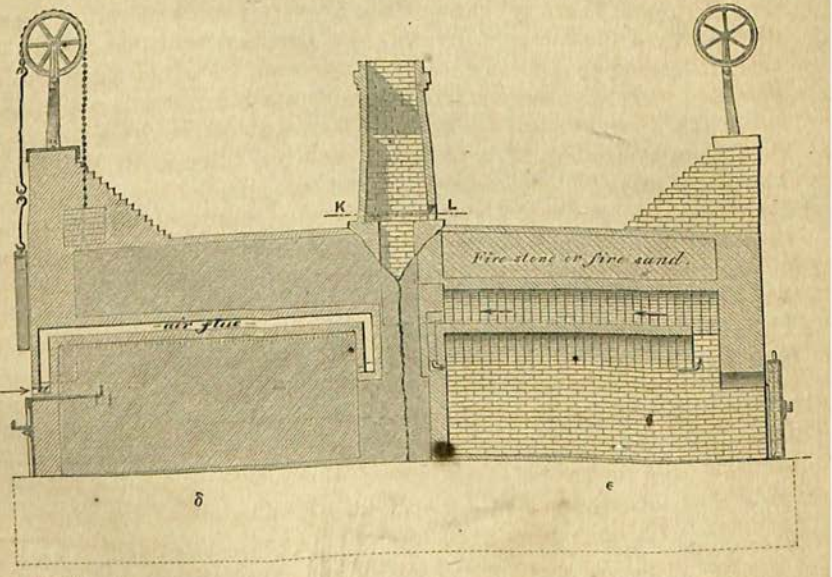

Fig. 27.
δ Section on the line A B, fig. 28. ε Section on the line C D E F, fig. 28.

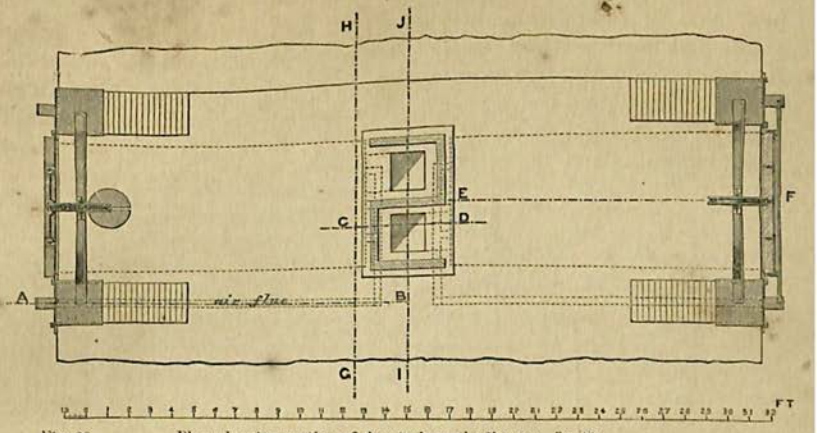

Fig. 28. Plan, showing section of the stack on the line K L, fig. 27

height, and the space enclosed by these walls and the stack at the back is filled with sand, so that a considerable amount of matter is thus accumulated, which will have the effect of retaining much of the heat generated during the process of coking. In the front and on the right of each oven is a flue, *a*, fig. 27 and fig. 28, which passes upwards, backwards, and downwards in succession, and then along the upper and back part of the oven (see the dotted lines in fig. 28), with the interior of which it communicates by three openings, *b b b*, fig. 26, β.

Between the front wall of the oven and the lower arch a space is left, as shown by the arrow in this part, fig. 27, ε. The space between the two arches communicates at the back with the stack. From the engravings it will be observed that the ovens are built back to back in double rows. There is but one stack to every two ovens; at a certain distance from the top it is divided by a partition wall (see fig. 26, γ), two flues being thus formed, one for each oven. Each of these flues is provided with an opening, and also with a sliding damper for regulating the draught: see fig. 27, L. The mouth of the oven is closed by a door, consisting of a frame of cast-iron filled with fire-bricks. The door may be conveniently raised or lowered by means of a chain passing over a pulley, and having a counterpoise weight attached to it. When lowered, it is securely fixed against the mouth by an iron bar placed transversely, as shown in fig. 26, γ. All these details will be sufficiently evident on an inspection of the engravings. The charge is introduced through the mouth, and, as usual, piled of the uniform depth throughout of 3 ft. 6 in. The door is then closed and luted. The air which supplies combustion enters the flue, *a*, and passes into the oven at the back, through the three openings, *b b b*. The products of combustion rise through the space in front of the lower arch, and then pass backwards into the stack through the space between the two arches, as may be clearly seen from the direction of the arrows in fig. 27, ε. These ovens are necessarily expensive in construction; but I am informed on good authority that they have been found in practice to be sufficiently advantageous to justify the outlay. The admission

of air can be surely regulated, and the amount of waste heat retained by means of the arrangement of the two arches with the superincumbent mass of matter effectually contributes to the coking of the next charge of coal. Under the impression that more sulphur is removed, the coke is quenched with water before drawing, the effect of which is to injure the bottom and increase the expense of repairs.

Mr. Parry, of the Ebbw Vale Iron-Works, informs me that he has recently (April, 1861) effected an important improvement in these ovens which is especially adapted to the coking of small coal. In the wall at the back are four vertical flues, in connexion with four flues immediately under the bottom, in the direction of its length. The air which sustains combustion is admitted, as in Jones's oven (fig. 29), only at the front into the space between the two arches (fig. 27, ε), and not below the lower arch into the chamber containing the coal. The gases evolved are thus burned on the outside of this chamber, and the gaseous products of combustion pass backwards and then downwards through two of the flues at the back, and from thence forwards through two of the flues under the bottom, returning by the other two flues under the bottom, and ascending through the other two flues at the back into the stack. No flame appears at the top of the stack, which is the case in the old ovens; so that all the heat developed by the combustion of the gaseous products is applied advantageously in the coking process. By this arrangement 50 per cent. more small coal can be coked at a time and with much greater economy than in the old ovens, as less coal is burned to waste than in those ovens. A stratum of small coal 4 feet thick may be uniformly coked to the bottom in the new ovens, whereas in the old ovens, in a stratum 3 feet thick, there was always a layer at the bottom, not less than 6 inches thick, of soft coke from imperfect carbonization.

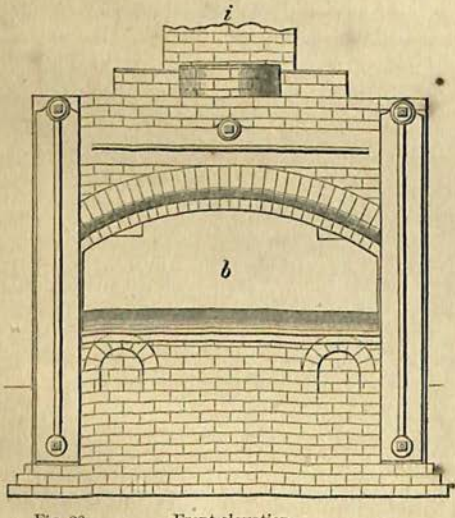

Fig. 29. Front elevation.

Jones's Coke-oven.—This oven was patented by the late Mr. Edward Jones, Manager of the Russell's Hall Furnaces, near Dudley, belonging to Mr. S. H. Blackwell. The annexed engravings were made from drawings prepared under the direction of my friend Mr. George Shaw, of Birmingham. The oven is built wholly of brick. The bottom is rectangular and flat, and inclines forwards and downwards from *a* to *b*, fig. 30. The sides and back are vertical; and above is an arch enclosing the top; at the front, *b*, is an arched opening, or mouth, which

may be closed by movable brickwork. In the centre of the arch forming the top of the oven is a circular opening, *s*; and at the back, *r*, is a narrow opening extending across: both these openings are closed with movable covers, around the edges of which sand is piled. In the back wall

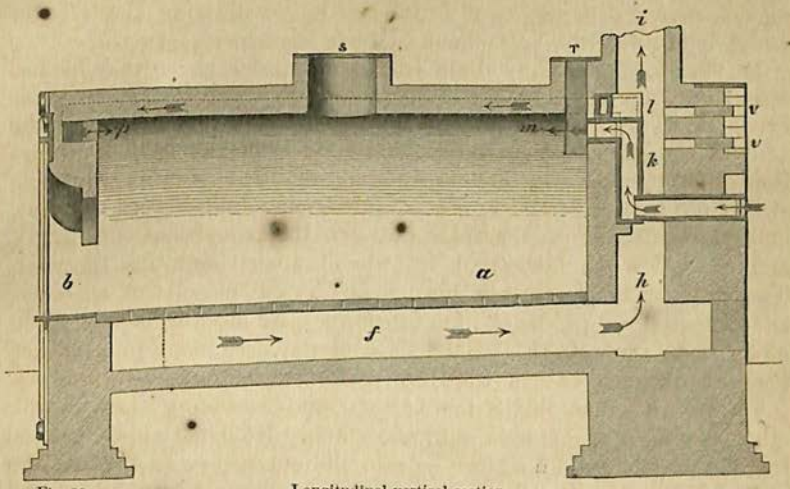

Fig. 30. Longitudinal vertical section.

there are two arched openings, *c*, *d*, fig. 32, from which flues pass downwards and forwards under the bottom, as shown by the arrows in fig. 33; and then, as shown by the arrows, *e*, *f*, in the same figure, to the back, where they communicate with the flues, *g*, *h*, which ascend into the chimney, *i*. The height of the stack above the oven is 8 feet; and the opening at the top is 14 inches square, and is provided with a damper. In figs. 29 and 31 are shown arched openings, by means of which the flues under the bottom of the oven may be cleaned out from time to time: they are closed with brickwork when the oven is in use. At the back are two cast-iron pipes, *k*, *l*, which communicate with the external air, and pass through the chimney, or stack, *i*: see fig. 30; the opening of each pipe is provided with a sliding iron damper: see fig. 31. The pipe *k*, after traversing the chimney, opens into the oven at *m*, fig. 30; and the pipe *l*, after rising to the top of the oven, opens into two flues, *n*, *o*, fig. 32, which pass forwards and enter the

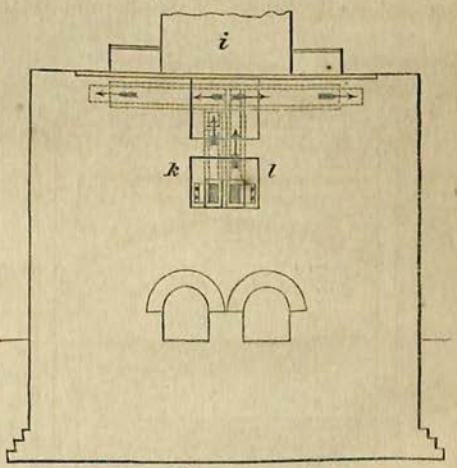

Fig. 31. End elevation.

oven through the opening at *p*, figs. 30 and 34. These flues should lie immediately upon the arch, and not at a distance from it, as shown in the engravings. At the back of fig. 30 are openings *v*, *v*, through which the inside of the oven and the pipes may be inspected: they are closed by movable bricks. In fig. 29 it will be observed that the bottom of the oven is at a considerable height above the foundation. This was rendered necessary by the badness of the ground on which the ovens were erected. The brickwork is suitably braced by cast-iron plates and wrought-iron tie-rods, as represented in fig. 29.

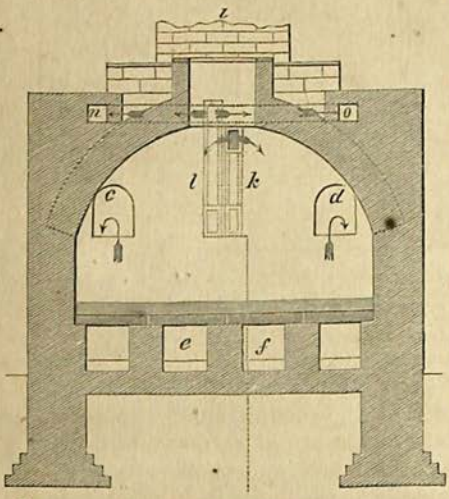

Fig. 32. Transverse vertical section.

About 4½ tons (1 ton = 20 cwt. of 112 lbs.) of the *thick coal* slack (the ten-yard seam) are mixed with 1 ton of coal-tar pitch, previously crushed between rolls, of which the upper one is fluted. This mixture is dropped into the oven through the opening *s* on the top, and spread evenly over the bottom. The mouth of the oven is then stopped by building up a wall of loose bricks. At some distance in front of this wall is placed a door of sheet iron, which is kept vertical by a transverse bar of iron suitably fastened at each end. Between the outside of the wall of bricks closing the mouth, and the inside of the sheet-iron door, a space is thus left, which should be well filled with coke-dust, *so that no air may enter the mouth of the oven*. When the oven is in use, it retains sufficient heat after one charge is drawn to ignite the next. The air to sustain combustion enters at the back through the cast-iron

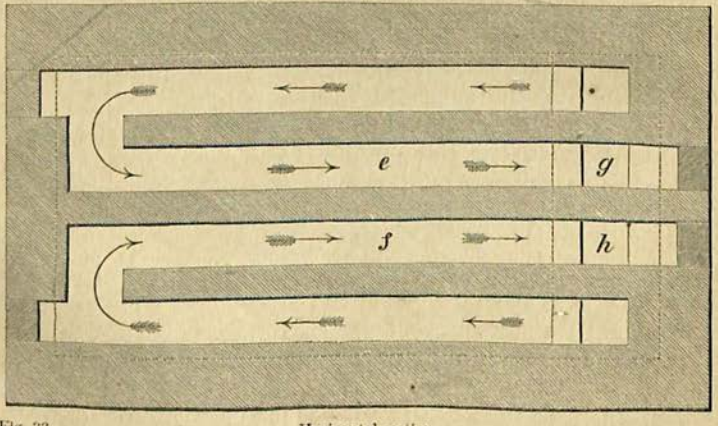

Fig. 33. Horizontal section.

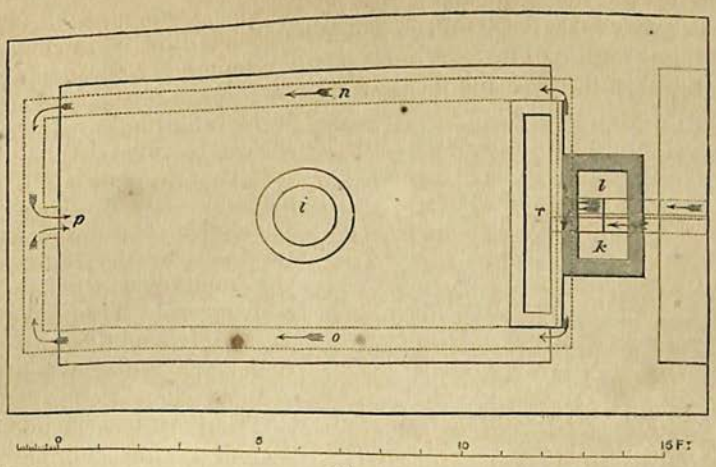

Fig. 34. Plan.

pipes *k l*, which are red-hot, so that it becomes much heated in its passage. One portion of the air enters at *m*, fig. 30, through the pipe *k*, while the other portion traverses the pipe *l*, and above becomes split into two currents, of which one passes to the flue *n*, and the other to the flue *o*, figs. 32 and 34. In front the currents unite and enter the oven at *p*. Heated air is thus supplied to effect combustion, and the amount can be exactly regulated by the sliding dampers, fig. 31. The volatile products of combustion escape through the openings *c d*, fig. 32, at the back, and from thence downwards, forwards, and backwards in succession, as shown by the arrows, fig. 33; from *e f* they pass into the stack through the ascending flues *g h*. By this arrangement the waste heat is applied to the heating of the bottom of the oven, so that the coal on the bottom may be subjected to distillation as in a retort. When in good working order, the interior of the oven will be observed, through the openings at the back, to be uniformly heated throughout to bright redness.

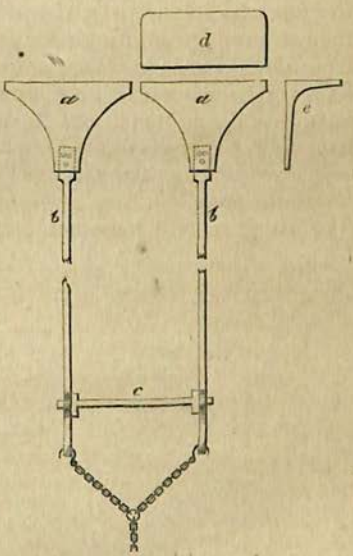

Fig. 35.

The charge is coked in 36 hours, when it might be drawn; but for the sake of convenience in arranging the division of labour, this is not done until after the lapse of 48 hours. After the completion of the process, the coked mass will be found to have receded more or less from the sides and back of the oven. Before drawing the temperature

of the oven is allowed to decrease considerably. The coke is drawn by means of drags, which are represented in fig. 35. The drag is formed of an iron casting *a*, and a handle or staff of good hammered iron *b*, about 13 feet long. The casting is in one piece, and consists of a horizontal plate *a*, from the broad end of which descends at right angles another plate *d*, which represents the end elevation. A side elevation of this casting is shown at *e*. At the free end of the staff *b* is a hole to receive a hook attached to a chain. There is also another hole through which enters the transverse bar *c*, which is provided with a collar near each end. Preparatory to drawing, two flat iron rods (1¾ in. broad and ¾ in. thick) are pushed along the top of the coke on one side to the back of the oven; and on these, which act the part of rails, one drag is made to slide until the depending flat part *d* may drop into the fissure produced by the recession of the coked mass from the back of the oven. The flat bars are then removed to the other side of the oven, and a second drag is introduced in the same manner. By means of a crowbar passed through the longitudinal opening *r*, fig. 34, in the top of the oven at the back, the fissure may when necessary be enlarged, and the adjustment of the drag thereby facilitated. In the engraving they are shown in the position which they occupy in the oven. They are pulled out by means of a windlass to which the chain in the figure is attached. They are kept parallel by the transverse bar *c*. The whole mass of coke is thus drawn at once, and immediately afterwards extinguished with water. By this arrangement there is no destruction of iron such as speedily occurs when the drag is left in the oven during the process of coking. There were two rows of these ovens, each containing ten; and on the top of each row, which is made level, there is a railway by which the coal may be conveniently carried to the charging holes.

The yield of coke was stated to be about 65 per cent. of the weight of the charge. The coke is firm and brilliant, and well adapted to iron-smelting. The actual cost of coking, exclusive of the cost of pitch, is estimated at 3½*d.* per barrow, or from 1*s.* 9*d.* to 2*s.* per ton of coke, short weight (1 ton = 20 cwt. of 112 lbs.). The price of pitch when I inspected these ovens in 1859 was 15*s.* per ton: it had risen previously. It was calculated that the slack virtually cost nothing, as it was paid for by the profit on the *coals* and *lumps* raised along with it.

The advantages of this process of coking are stated to be as follows:—1st. The introduction of air heated by the waste heat of the slack. 2nd. The air enters immediately under the arch, and as far as possible from the surface of the coal, whereby the volatile products evolved from the coal are effectually burned, and the loss occasioned by the combustion of the coke formed is reduced to the minimum; and 3rd. The method of drawing, whereby the destruction of the iron in the drags is completely avoided.

Mr. Jones informed me that he had tried experiments in covering the surface of the mixture in the oven with various matters, such as lime, blast furnace slag, &c., but without success on account of their

melting. I witnessed a first experiment of this kind with a mixture of the siliceous sifted residue of the Leighton-Buzzard iron ore and coke dust; and Mr. Jones was of opinion that the result was the most successful he had yet obtained. This ore consists chiefly of hydrated sesquioxide of iron mixed with sand.

When the bottom of a coke-oven is heated by flues underneath, the mass of coke is always divided into two distinct strata, and the line of separation between them is stated to be that of *least* heat.

Coke-oven of the Brothers Appolt.—The following description is to a great extent a literal translation from that published by the inventors.[4]

With the addition of certain modifications which experience has shown to be useful, this description applies to an oven at the works of Messrs. Pinart, Brothers, at Marquise, in the department of Pas-de-Calais, in France, which was first lighted on the 1st September, 1857.

It consists essentially of a large rectangular brick chamber $5^m\,23$ (about 17 feet) long, $3^m\,49$ (about 11 feet 6 inches) wide, and $4^m\,00$ (about 13 feet) high. It is divided by partition walls $0^m\,12$ (about $4\frac{3}{4}$ inches) thick, into a series of twelve compartments, *k*, *k*, &c., each of which may be regarded as a distinct oven, or kiln, $1^m\,24$ (about 4 feet) long, and $0^m\,45$ (about 1 foot 6 inches) wide at the base, and $1^m\,12$ (about 3 feet 8 inches) long and $0^m\,33$ (about 13 inches) wide at the upper part. Each compartment has its own walls, and is surrounded by a free space from top to bottom, fig. 36, *i*; and all the similar spaces thus existing round the twelve compartments are in free communication, forming in reality one continuous space. The average distance between the corresponding walls of neighbouring compartments is from $0^m\,20$ (rather more than $7\frac{3}{4}$ inches) to $0^m\,25$ (rather more than $9\frac{3}{4}$ inches). The series of compartments is contained within four vertical walls of fire-brick, between which and the mass of brick-work on the outside is a space, *e*, filled loosely with pulverized matter, which is a bad conductor of heat, and which will in a certain degree permit the dilatation of the brick-work within. All the compartments are connected solidly together by strong fire-bricks, *b*, *b*, &c., extending across the spaces, *i*, *i*, &c., and placed quincuncially in the partition walls and the surrounding vertical walls: there are 60 of these bricks in each compartment. At the top of each compartment is an opening, o, fig. 36, formed by the walls on the short sides rising vertically, and the walls on the long side approximating upwards in a series of steps; and at the bottom is an opening, *p*, provided with a cast-iron door. The partition walls of the compartments rest upon frames of cast-iron, fig. 36, *u*, $0^m\,03$ (about an inch) in thickness, which are supported in the direction of their length by brick arches $0^m\,24$ (about $9\frac{1}{2}$ inches) wide. These arches are so arranged

o o
o
o o

[4] Annales des Mines, 5. s. T. 13, p. 417.

that an open space is left under each compartment. Instead of arches cast-iron bearers may be employed. The bottom of the free spaces is covered with fire-brick to the height of $0^m 27$ (about $10\frac{1}{2}$ inches) above the frame-work of cast-iron. Under the compartments and in the direction of their short axes two parallel passages arched at the ends extend through the building. The outer walls of the oven are vertical up to the frame-work of cast-iron, from which they incline inwards to the top. The cast-iron doors which close the compartments at the bottom are $0^m 02$ (about $\frac{3}{4}$ inch) thick. Each door is strengthened by three transverse bars of wrought-iron, by means of which it is firmly fixed to an iron rod supported at each end by a staple let into the under side of the cast-iron frame. A hinge is thus formed. The end of the suspending rod which is directly towards the long side of the oven is prolonged, and the projecting part is squared so that it may be turned by a key like that of a piano. In the centre and passing through the middle transverse bar of the door is a pivot, and on this turns a flat bar, of which the ends may slide into grooves in pieces projecting from the under and short sides of the cast-iron frame: the door may thus be securely fastened. It may be shut by a key, which passes through an iron pipe built in the brick-work and

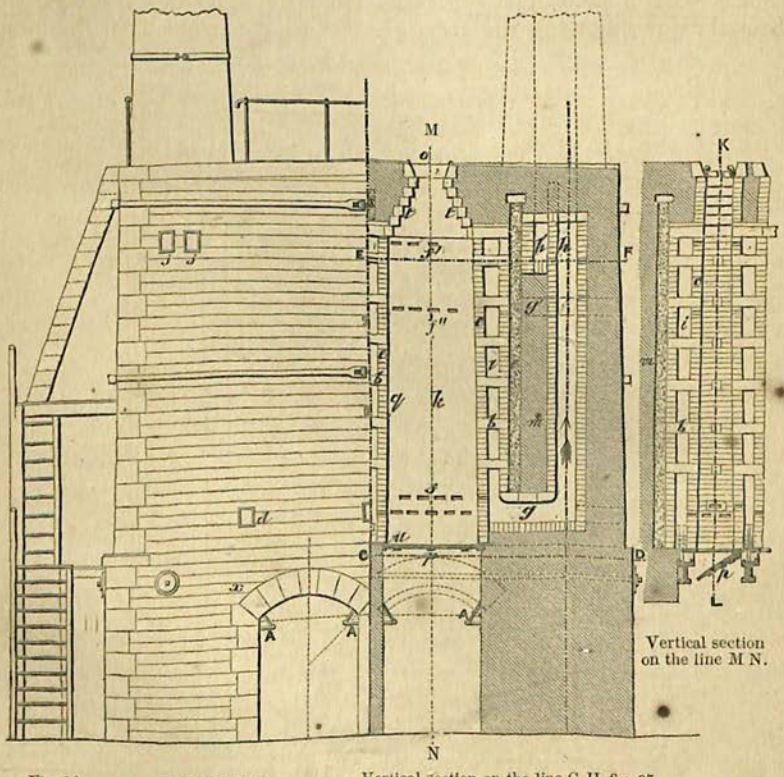

Fig. 36. Front elevation. Vertical section on the line G H, fig. 37.

firmly fastened to the iron frame, that it may not turn round with the key.

In a space included between the vertical heights of 0^m 42 (about 16 inches) and 0^m 57 (2 feet) from the bottom, the partition walls of each chamber are traversed by two rows of small horizontal openings 0^m 14 ($5\frac{1}{2}$ inches) long and 0^m 02 (about $\frac{3}{4}$ inch) high, fig. 36, *f*: there are nine such openings on each long side and three on each small side. At the upper part there are three similar openings on each long side only, *f'*. Through these openings the volatile products evolved during the coking of the coal pass into the surrounding open surfaces, in which they are burned by atmospheric air admitted through holes in the long sides of the oven. It is asserted that the heat thus developed more than suffices to coke the whole coal from which these volatile products have been derived.

Experience has proved the utility of the small openings, *f'*, at the upper part or somewhat lower, as at *f''*; for in operating upon certain coking coals, if the whole of the tar evolved is obliged to traverse the lower part of the cake of coke, too much carbon may be deposited, and the descent obstructed. The height of all the small openings, *f*, *f'*, is purposely restricted to 0^m 02 (about $\frac{3}{4}$ inch) in order that the fine coal may only produce a small talus; and in the event of their becoming choked with little stoppers of coke, the latter may be withdrawn of themselves in following the mass of coke as it shrinks. In the long

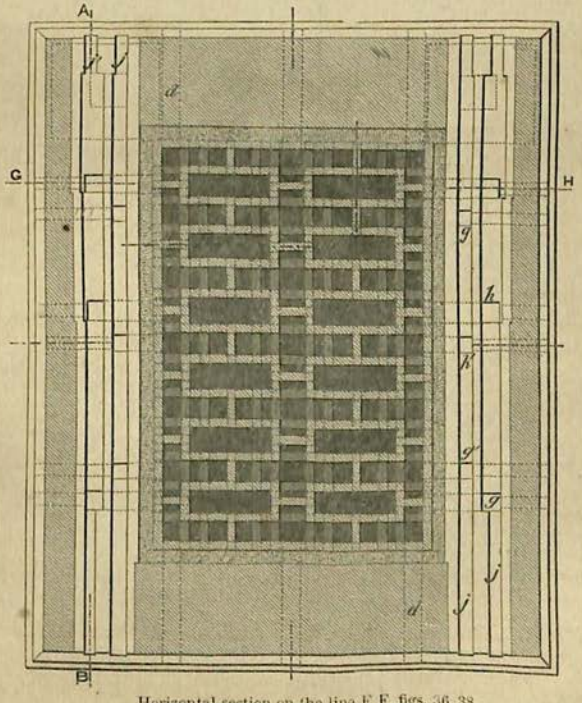

Fig. 37. Horizontal section on the line E F, figs. 36, 38.

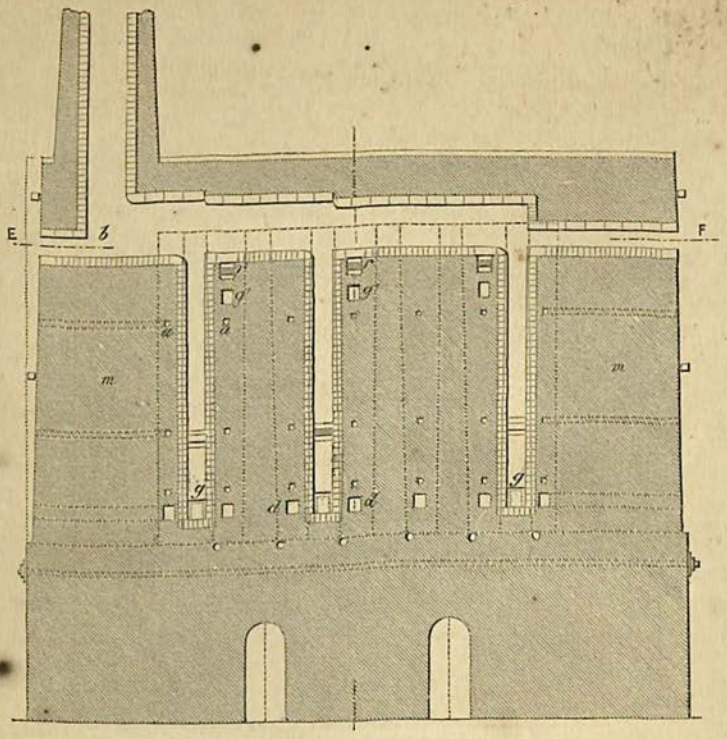

Fig. 38. Longitudinal section on the line A B, fig. 37.

side walls of the oven are the flues, g, g', which receive the products of combustion from the spaces surrounding the chambers and convey them to the stacks. There are twelve in all—three below and three above in each of these walls. Those below are square in section, $0^m 25$ (about $7\frac{3}{4}$ inches) on the side; at first they pass horizontally to the middle of the outer brick-work, then ascend vertically and open into a horizontal flue, h. Those above are $0^m 20$ (about $7\frac{3}{4}$ inches) long by $0^m 17$ (about $6\frac{1}{2}$ inches) broad; they also pass horizontally into the outer mass of brick-work, ascend vertically, and open into a second horizontal flue, h', parallel to the first. All these vertical flues have dampers of fire-brick at the top, so that the draught may be regulated at will. The four horizontal flues, of which there are two on each side, g, h, have all the same height of from $0^m 54$ (about 1 foot 9 inches) to $0^m 67$ (about 2 feet 2 inches). Into the two outer flues—of which the width is from $0^m 25$ (nearly 10 inches) to $0^m 29$ (nearly $11\frac{1}{2}$ inches)—open the six vertical flues from below; and into the two inner flues—of which the width is $0^m 17$ (about $6\frac{3}{4}$ inches)—open the six flues leading from the compartments at the top. The two horizontal flues on each side are separated by a wall of the width of a single brick, and open into a stack of which the internal sectional area is a square, $0^m 48$ (about 1 foot 7 inches) on the side, and the height

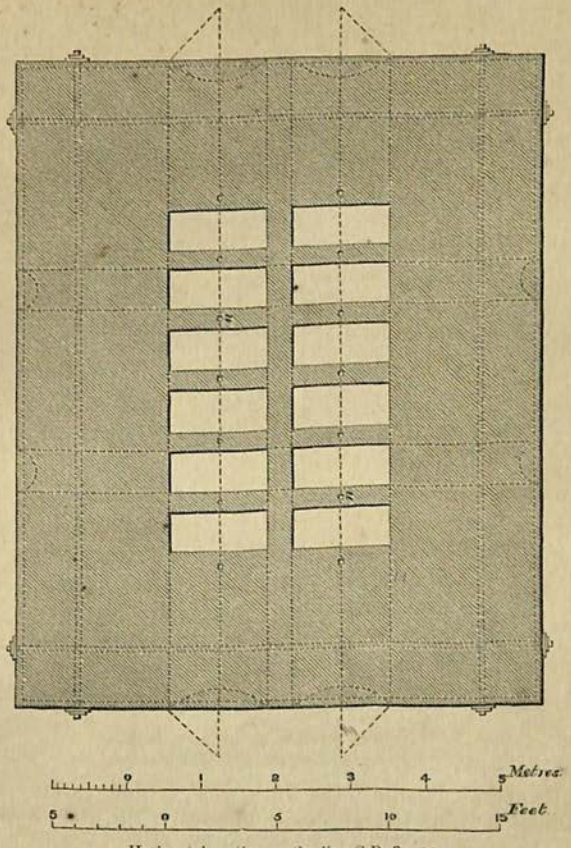

Fig. 39. Horizontal section on the line C D, fig. 36.

above the top of the oven 5^{m} 00 (about 16 feet 6 inches). There are two stacks, one on each side, fig. 36; in the section the position of one of the stacks is indicated by dotted lines. The lower part of the stacks within, to the height of 1^{m} 00 (about 39 inches), is divided by a partition of single brick into two parts, corresponding to the horizontal flues which open into them. At *j*, *j*, are openings with iron frames, by means of which the horizontal flues may be cleaned out. It is hardly necessary to remark that every part of the oven exposed to a great heat should be made of fire-brick.

The free spaces surrounding the compartments are closed at the top with two courses of fire-brick, upon which is ordinary brick-work of sufficient thickness to prevent the loss of too much heat. A few hollows may be left in the brick-work to allow for the effect of expansion by heat, as shown at *s*, fig. 36. The platform on the top of the oven is slightly inclined towards the two long sides, and is covered with cast-iron plates. The bottom of the free spaces may be cleaned out from the outside of the oven through openings *d*. There are small open-

ings provided with sliding registers through the brick-work, *a*, which answer the double purpose of supplying air to effect combustion, and of enabling an inspection to be made of the interior of the oven. There are also other small openings, *n*, for the admission of air, through the arches upon which the long sides of the compartments are built. The brick-work is held firmly together by suitable iron tie-rods, as shown in fig. 36.

The oven is charged at the top, and the coke is withdrawn at the bottom and removed in iron waggons. In order to prevent the coke from falling with too much force into the waggon, inclined and projecting plates of cast-iron are fixed in the walls underneath each compartment, fig. 36, A. The mass of coke lodges on these plates, from which it may be detached in pieces and carried away.

Mode of conducting the process.—The oven is supposed to be new and ready for lighting. At the bottom of each compartment a temporary grate of iron bars is adjusted; and the sides, to the height of $0^m 3$ (about 1 foot) above the grate, are lined with fire-bricks placed slanting, in order to prevent the adhesion of the clinker produced in heating the furnace in the first instance to the walls of the compartment: a moderate fire is made, and kept up by throwing in coal at the top, which is allowed to remain open until the walls of the compartments have become red-hot. When this occurs, it is generally kept closed; so that the flame from the temporary grate is compelled to escape through the small openings leading into the surrounding free spaces, and all the interior of the oven is thereby heated. By only partially opening the registers of the air-flues a portion of the products of combustion will escape through the outer walls of the oven, and promote their desiccation. After eight or ten days' firing, gradually increased, the oven will be found to have attained the temperature of from 1200° to 1400° C., which is necessary for the commencement of the charging. In order always to insure an equable degree of heat through the oven, and to simplify the management of the latter by the registers and air-flues, it is expedient to charge the two series of compartments alternately. The temporary grate and brick-lining at the bottom is removed from the compartment which it is proposed to charge. The door is closed and securely fixed in the manner previously described, and then covered with a layer of coke-dust about $0^m 30$ (about 1 foot) thick: this is done to protect the door from heat, to close effectually the bottom of the compartment, and to prevent loss of heat. The charge of coal is now introduced, and a cover placed over the top luted with coke-dust or clay.

The gases which are immediately evolved when the coal comes in contact with the red-hot sides of the compartment pass into the surrounding free spaces, where they are burnt, and so sustain the heat of the oven. An hour afterwards the second compartment is charged in like manner, and so in succession until all have been charged. As the amount of gas produced increases during the day with the number of charges, it is necessary to open the registers, and all that is required to be done during the night is gradually to shut them again

in proportion as the evolution of gas decreases. Carbonization being completed at the end of twenty-four hours, on the following day the coke is drawn from the first compartment at the same time as the charging took place on the previous day. Immediately afterwards the compartment is charged again.

The process is thus continued without interruption, the coke being drawn from each compartment twenty-four hours after it has received its charge of coal. No inconvenience arises from the use of washed coal which still retains moisture. By suitably decreasing the admission of air and the exit of gases from the oven, the charging may be omitted on particular days; and yet the heat will continue sufficiently high to enable the charging to be effected on the following day.

Principles on which the oven is constructed.—During the process of coking each compartment is in reality a closed vessel, with the exception of the apertures through which the volatile products escape into the surrounding space; and in so far it resembles a gas-retort. No air from without can reach the interior of a compartment, even though cracks may be produced in its walls. In this respect it differs essentially from ordinary coke-ovens, into which air is allowed to enter above the coal undergoing carbonization. If from neglect of the workmen or other circumstances too much air passes into these ovens, a considerable amount of coke may be needlessly consumed; whereas in the Appolt oven this evil cannot occur. By the subdivision of the oven into a series of compartments, each of which is surrounded by burning gas, a very great extent of heating surface is obtained, which in the oven described is nearly 190 square metres for a charge of 17,000 kilogrammes of coal,—a surface two or three times greater in proportion than that of the most improved kinds of other ovens. As the coke is divided into masses of but little width, it can be readily penetrated by heat, and, therefore, subjected to *rapid* carbonization. The combustion of the gases in these ovens is stated to be more perfect and active than in ordinary ovens, because air enters through numerous openings in the outer walls of the oven, and the mixture of air and gases freely circulates through a large extent of space. This result is further promoted by the exit of the jets of gas through numerous small openings, and, in consequence, its more rapid and complete admixture with air. The partial exit of gas from the lower part of each compartment obviously tends to produce an equable diffusion of temperature through every part of the oven. The changes of temperature which occur in other ovens, from the charging of the coal to the drawing of the coke, are avoided; for, as the charging of the compartments takes place at successive intervals in a well-arranged order, the heat of the oven is maintained at nearly the same degree during the whole course of the operation. The heating surface of this oven, compared with its external surface of brick-work, is greater than in other ovens, and, consequently, much less heat is lost by cooling from without. The vertical position of the compartments is said to be important, as presenting the following advantages: it is possible only by this means to secure the advantageous relation between the heating and cooling surfaces, so that a large quantity of

coal may be coked in a proportionately limited space—in respect of its relative power of production it occupies much less space than other ovens—as there is no arch exposed to the action of heat, the oven is more solid, and the coke in dropping down exerts no injurious amount of wear of the sides—as the charging and drawing may be very quickly effected, the walls of the compartments are less liable to be cooled during these operations—the pressure of the column of coal produces a coke of much greater density than that obtained in other ovens.

Actual results obtained in coking by this method.—At the date of the publication of Messrs. Appolt's description, June, 1858, the oven at Marquise, having worked regularly and without the least interruption since the time it was lighted on the 1st of September, 1857, yielded the following results. Each compartment contained from 1350 to 1400 kilogrammes, that is, somewhat less than 1½ tons of coal (1 ton = 20 cwt. of 112 lbs.). The coking was completely effected in the course of twenty-four hours. The workmen suffered not the slightest inconvenience in the operations of charging and drawing, which took place in the day-time. I should have expected otherwise. The service of four men was required. Belgian caking coal gave from 80 to 82 per cent. of coke, and English caking coal from 72 to 73 per cent. This yield is stated to be from 10 to 12 per cent. greater than that of ordinary ovens. Mixtures of non-caking and caking coals in different proportions also gave good results. The first experimental oven was erected at St. Avold, department Moselle, France, by which the correctness of the principles of the method was established. Another larger experimental oven was subsequently built in the centre of Sarrebrück coal-field in Prussia; and although it did not possess several of the contrivances which have since been adopted, yet the result was satisfactory. An oven had been previously erected at Rive-de-Gier in 1856, and continued at work regularly during several months, by which the maximum yield and solidity of construction were established; but it was afterwards discontinued, as the labour was found too expensive, from there being only six compartments. The coke produced at Marquise was used in the iron-smelting furnaces of that establishment, and was admitted to be of very good quality—hard, dense, close-grained and possessing all the characters of good coke for metallurgical purposes. It was demonstrated that the quantity of gas evolved during coking was far more than sufficient to effect carbonization and to maintain the heat of the oven at the proper degree, so that the excess of gas might be advantageously applied to raise steam, &c. Under ordinary circumstances the cost of erection of an oven like that of Marquise may be estimated at from 14,000 to 15,000 francs,—that is, from 560*l.* to 600*l.*

Remarks.—This oven differs much in construction from all other coke-ovens, and appears completely to fulfil the conditions of a close vessel or retort. Now it has been previously stated that the non-caking thick coal of South Staffordshire will cake and produce a solid coherent coke, provided it be rapidly exposed to a high temperature in a perfectly close vessel. My friend Mr. Samuel Blackwell, of Dudley, some years ago informed me of this fact, about which, I

confess, I was at first somewhat sceptical. However, I visited Mr. Blackwell's works, and saw the experiment made to my entire satisfaction. A Hessian crucible five inches deep was nearly filled with powdered thick coal slack, which was pressed well down and then plastered over with wet clay. In this state the crucible was put into Jones's coke-oven, described p. 162, through one of the holes at the back, and there exposed to a bright red heat during twenty minutes or half an hour, when it was withdrawn and allowed to cool. A perfectly solid coke was produced. The exclusion of the air by clay is essential; and it was this which suggested the experiment of covering the surface of the coal in the oven, as recorded at p. 166.

To the coal-masters of South Staffordshire an economical solution of the problem of coking the thick-coal slack would be of immense value. A prodigious amount of the fine slack has been and still continues to be left in the pits, because it cannot be raised with profit. I have no doubt that should any person be so fortunate as to succeed in converting this at present worthless material into good coke at a moderate cost, he would realize a large fortune; and he would, moreover, have the satisfaction of prolonging the industrial life of South Staffordshire, which has begun to suffer from the exhaustion of its fuel. In 1854 a patent was taken out by Mr. Dawson for converting coal-dust and coke into solid blocks of fuel.[5] The dust, moistened with water, is pressed into a cast-iron box having a tightly-fitting cover, and the whole is exposed to a temperature ranging from 300° to 700° Fah. An experimental oven was erected near Whitechapel, which I visited. At my request, Mr. Dawson operated upon some of the thick-coal slack from West Bromwich, with which I supplied him; but the result was unsuccessful. Whether the Appolt oven will satisfactorily realize the conditions essential to the coking of this slack, experiment alone can determine. It is a costly structure, it must be admitted: nevertheless, according to the statement of the inventors, the cost is less in proportion to yield than in other coke-ovens. Inventors are apt to be sanguine, and often in good faith ascribe merits to their inventions which experience proves either to have had no existence, or at least to have been much exaggerated. We must, therefore, be cautious in admitting without further confirmation all the advantages enumerated by the Messrs. Appolt in favour of their oven.

Composition of the waste Gases of Coke-ovens.—We are indebted to Ebelmen for analyses of the gases of coke ovens at Seraing in Belgium.[6] The floor of the oven is a rectangle terminated at each end by a trapezium.[7] The roof is cylindrical above the rectangle, and conical above the trapeziums. There are three chimneys in a line: one in the centre of the cylindrical part of the roof, and one on each side at the junction of the cylindrical with the conical part of the roof. The area of the central chimney is double that of each of the others. The three chimneys are never in use at the same time: the two lateral chimneys

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[5] Specification, A.D. 1854. No. 3.

[6] Recueil des Trav. Scient. 2, p. 142. Vid. Traité Théor. et Prat. de la Fabrication de la Fonte. Par B. Valerius, 1851, p. 255.

[7] This oven is described in detail at p. 182.

are closed when the central one is open, and conversely. The central chimney conducts the gases which escape from the oven under the boiler of a steam-engine. Caking coal was coked in these ovens, which yielded 80 per cent. of coke, consisting of 78 parts of carbon and 2 of ashes, and 20 per cent. of volatile matters. Ebelmen gives no elementary analysis of this coal, but inferred its composition from that of a coal at Rochebelle, near Alais, which yielded very nearly the same per centage of coke, namely, 78, and of which the following analysis was made by Regnault:—

Carbon	89·27
Hydrogen	4·85
Oxygen and nitrogen	4·47
Ashes	1·41
	100·00

The charge for each oven is 3 cubic metres (= 2750 kil., or 2 tons 14 cwt. 16 lbs.) of small coal, which is spread as evenly as possible over the floor, forming a stratum about 0^m 33 (= 12·99 inches) in thickness. All the chimneys are open at a time for the comfort of the workmen. When the charging is over, the lateral chimneys remain open while the central one is closed, and continue so for two or three hours; the doorways are closed, but not luted, and carbonization commences. It may be divided into three stages, as follows: in the first stage, which lasts about three-quarters of an hour, there is only disengagement of water; in the second stage, which lasts about an hour and a half, the gases take fire and partially burn with a very smoky red flame, the chimneys remain wide open, and the doorways are closed, but not luted; in the third stage, the gases burn well with a smokeless white flame. The coal appears incandescent to the depth of 8 or 10 centimetres (3 to 4 in.) from the surface; the doors are then luted, and only a small fissure is made in the clay luting at the upper part. The lateral chimneys may now be closed, and the central one entirely opened. When the flame begins to decrease, the fissure in the clay luting is gradually contracted and at last completely stopped, and when flame ceases the chimney is closed. The period of coking, inclusive of charging and drawing, lasts from 22 to 24 hours. The average yield of coke is 160 per cent. in volume, and 67 per cent. in weight. Ebelmen analysed the gases collected from these ovens at three different stages of the process, and obtained the following volumetrical results:—

	1.	2.	3.	Mean.
Carbonic acid	10·13	9·60	13·06	10·93
Carbonic oxide	4·17	3·91	2·19	3·42
Marsh gas (CH^2)	1·44	1·66	0·40	1·17
Hydrogen	6·28	3·67	1·16	3·68
Nitrogen	77·98	81·16	83·25	80·80
	100·00	100·00	100·00	100·00
Ratio between the volume of oxygen combined with carbon and 100 vols. of nitrogen	15·7	14·2	17·0	15·6

1. Gas collected two hours after the kindling of a charge from one of the lateral chimneys of an oven; smoke black and dense; reddish flame appearing at intervals. 2. Gas collected 7½ hours after charging; bright, but still somewhat reddish, flame, without smoke. 3. Gas collected after 14 hours' coking; flame clear, but of little volume; carbonization being apparently near completion.

The relation in weight between the elements contained in the gas of mean composition is as follows:—[a]

Carbon	In carbonic acid	1·408	2·004
	In carbonic oxide	0·443	
	In marsh gas	0·153	
Oxygen	In carbonic acid	3·758	4·348
	In carbonic oxide	0·590	
Hydrogen	In a free state	0·079	0·130
	In marsh gas	0·051	
Nitrogen		24·353	
		30·835	
Oxygen which has disappeared, as deduced from the ratio existing between nitrogen and oxygen in atmospheric air			2·925

24·353 of nitrogen are associated with 7·273 of oxygen in atmospheric acid: hence, 7·273 − 4·348 = 2·925.

The per centage of coke obtained in these ovens was 67, so that 33 per cent. of the coal had been removed either by volatilization or combustion. Now, supposing that the 67 per cent. of coke consisted only of 65 parts of carbon and 2 of ashes, it follows that the 33 per cent. of matter lost by coking contained the following elements:—

Carbon	23·68
Hydrogen	4·85
Oxygen and nitrogen	4·47
	33·00

The relation in weight between the carbon and hydrogen is 1 : 0·205; but the relation in weight between the carbon and hydrogen deduced from the mean composition of the gases above stated is 1 : 0·065. Hence, Ebelmen draws the conclusion that more than two-thirds of the hydrogen contained in the coal are burned during the process of coking. He remarks, however, that in this computation no account is taken of the amount of tar and other condensable matters evolved during the process; but he considers that, in consequence of the very high temperature of the oven during nearly the whole period of coking, the proportion of condensable products is of little account, and that it is only at the beginning of the operation that they are disen-

[a] Data from which these calculations have been made at 0m.760 (= 30 in.) and 15° 5 C. (60° F.):—

	Grains.
100 cubic inches of carbonic acid weigh	47·26
,, carbonic oxide ,,	30·21
,, oxygen ,,	34·29
,, hydrogen ,,	2·14
,, marsh gas ,,	17·41
,, nitrogen ,,	30·14

gaged in appreciable quantity. It must be borne in mind that the data from which Ebelmen draws his conclusion involve an assumption as to the composition of the coal of which no analysis was made.

The volume of oxygen existing in combination in the gas of mean composition is to that of the nitrogen as 15·63 : 100; whereas the relation in volume between the oxygen and nitrogen which entered the oven in the state of atmospheric air is as 26·26 : 100. The difference, 10·63, represents the volume of oxygen which has served to burn the hydrogen. Hence two-fifths of the oxygen of the air introduced into the coke-oven have been converted into water. In this calculation Ebelmen remarks that the small amount of oxygen contained in the coal has been neglected, but that the correction required to be made in consequence will in no way affect the conclusions enunciated.

The quantity of atmospheric air which the process of coking will require may also be deduced from the composition of the gases. The relation in weight between the nitrogen and carbon in the gas of mean composition is 12·2 : 1. Atmospheric air contains 77 per cent. of nitrogen by weight; consequently, for 1 part by weight of carbon in the gases, 15·8 of air will enter the oven. Now, it has previously been stated that the quantity of carbon carried off in the gases is 23·68 per cent. of the weight of the coal; the weight of air, therefore, introduced during the process of coking is to that of the coal as 3·74 : 1. Hence, in coking 2 tons 14 cwt. 16 lbs. (= 2750 kil.) of coal, not less than 10 tons 2 cwt. 55 lbs. of air will be required, or in volume 296188 cubic feet (100 cubic inches of air weighing 31·0117 grains). Supposing the duration of the coking process to be 24 hours, 12341 cubic feet of air (1 lb. of air = 13·06 cubic feet) will enter the oven per hour, very nearly 205·7 cubic feet per minute, and 3·43 cubic feet per second. Ebelmen estimated that this amounted to about two-thirds of the air blown into a charcoal iron-smelting furnace yielding 2 tons of pig-iron in the 24 hours.

Economic application of the waste Gases of Coke-ovens.—From the data which Ebelmen obtained in his investigation concerning the composition of the gases of the coke-ovens at Seraing may be approximately calculated the amount of heat produced during the process of coking, as well as the amount which may be further developed by the complete combustion of the carbonic oxide, hydrogen, and marsh gas existing in those gases. Ebelmen made such a calculation, and came to the conclusion that two-thirds of the heat capable of being evolved by the complete oxidation of the volatile products were rendered sensible in the ovens, and only one-third remained to be generated by the subsequent oxidation of the combustible constituents of the gases which escaped from the ovens.

Suppose that the coal employed yielded 67 per cent. of coke, and 33 per cent. of volatile products, consisting of 4·85 of hydrogen, 23·68 of carbon, 2·97 of oxygen, and 1·50 of nitrogen; and grant that only the amount of hydrogen in excess of what is required to form water with the oxygen in the coal is available as a source of heat, namely 4·479. In 1 part by weight of coal, 0·04479 of hydrogen and 0·2368 of

carbon will suffer combustion; and the number of units of heat which will be evolved by the conversion of the hydrogen into water and the carbon into carbonic acid will be respectively 0·04479 × 34000 (calorific power of hydrogen) = 1522·860, and 0·2368 × 8080 (calorific power of carbon) = 1913·344. But as the water formed from the hydrogen will pass off as steam at the temperature at least of 100° C., it is necessary to deduct the latent heat of that steam; for it will be remembered that in the determination of the calorific power of hydrogen in the calorimeter, the vapour of water produced is condensed, and its latent heat rendered sensible. Not only must the latent heat of the steam, resulting from the combustion of hydrogen in the oven, be deducted, but also that of the water which is supposed to exist in the coal. Hence the total amount of latent heat to be deducted is 0·0485 × 9 × 537 = 234·400. The greatest number of available units of heat from the hydrogen will, consequently, be 1522·860 − 234·400 = 1288·460; and the sum of the units from the hydrogen and carbon in 1 part by weight of coal will be 1288·460 + 1913·344 = 3201·804.

The number of units of heat resulting from the combustion effected within the oven during the coking process is easily found. The total quantity of carbon in the volatile products of 1 part by weight of coal is 0·2368; for 100 parts of coal yielded 33 per cent. of such products, of which 23·68 consisted of carbon. Now, in a volume of the gases of the coke-ovens at Seraing which contained 2·004 parts of carbon by weight, 1·408 were present in carbonic acid, 0·443 in carbonic oxide, and 0·153 in marsh gas. Hence, of the total 0·2368 of carbon in the volatile products from 1 part by weight of coal, 0·1664 existed in carbonic acid, 0·0523 in carbonic oxide, and 0·0181 in marsh gas. The carbon and hydrogen in this gas may be regarded as in a free state; as its calorific power is nearly the mean of the calorific powers of its components. The number of units of heat resulting from the combustion of carbon in the oven is $\overline{0{\cdot}1664 \times 8080} + \overline{0{\cdot}0523 \times 2473}$ (the calorific power of carbon when the product of its combustion is carbonic oxide) = 1473·850.

The number of units of heat which will be evolved by the perfect combustion of the carbonic oxide, hydrogen, and marsh gas in the gases escaping from the ovens, may also be found in a similar manner. The relation in weight between the carbon and hydrogen in those gases is 2·004 : 0·130; and the relation in weight between the hydrogen existing in a free state and combined with carbon is 0·079 : 0·051. Hence, in the volatile products from 1 part by weight of coal, 0·0933 of hydrogen will be free, and 0·0603 combined; and as the combined hydrogen may, for the reason assigned above, be regarded as free, the number of units of heat which will result from the combustion of the hydrogen is $\overline{0{\cdot}1536 \times 34000} - \overline{0{\cdot}1536 \times 9 \times 537}$ (latent heat of the steam produced) = 448·0051. The number of units of heat which will be developed by the combustion of carbonic oxide is 0·0523 × 5607 = 293·246; and by the combustion of the carbon combined with hydrogen, 0·0181 × 8080 = 146·248.

From the preceding data it appears that the total maximum number

of units of heat, capable of being evolved from the perfect combustion of the carbon and hydrogen, separated from 1 part by weight of coal during the process of coking, is 3201·804. Now, by deducting from this number the sum of the number of units of heat resulting from the combustion of carbon in the oven (1473·850), and of the number yet to be evolved on the complete combustion of the gases as they escape from the oven (887·4992), we obtain the number of units of heat which is evolved by the combustion of hydrogen in the oven, namely, 840·455. The number of units of heat, therefore, actually evolved during the process of coking 1 part by weight of coal, is 1473·850+840·455 = 2314·305. Hence the ratio between the number of units of heat evolved and that which remains to be evolved is nearly as 2 : 1. The maximum number of units of heat capable of being developed during the coking of 2750 kil. of coal is 8804961, of which 2440622 may be made available by the combustion of the gases escaping from the oven.

The preceding approximate calculations must be correct, if the data upon which they are founded be true. But let us now inquire whether we have reason to doubt the truth of these data. In the gas of mean composition, 24·353 parts by weight of nitrogen were associated with 4·338 of oxygen, which existed in combination with carbon. But in atmospheric air the same weight of nitrogen is associated with 7·273 of oxygen; and as the nitrogen present in the gas was derived from atmospheric air, it follows that 7·273 − 4·338 = 2·925 parts by weight of oxygen have disappeared in consequence of its combination with hydrogen and the formation of an amount of water containing 0·3656 parts by weight of hydrogen. The relation in weight between the oxygen which has disappeared and the carbon in the gas of mean composition is 2·925 : 2·004. Hence the relation in weight between the oxygen which disappears in the coking of 1 part by weight of coal and the total weight of carbon separated is 0·3456 : 0·2368. But 0·3456 of oxygen requires 0·0432 of hydrogen, which would evolve 1468·800 − 208·786 (latent heat of steam produced) = 1260·014 units of heat. Now, according to the previous calculation, the number of units of heat evolved by the combustion of hydrogen in the oven is 840·455. It may, therefore, be inferred that the data of Ebelmen cannot all be true. The composition of the coal, and the weight and elementary composition of the volatile products separated during the process of coking, may be exactly determined; but it must, obviously, be very difficult to arrive at the correct average composition of the gases evolved during the whole process of coking. The three specimens of gas which Ebelmen collected at intervals of 2 hours, 7½ hours, and 14 hours after the commencement of the process, are assuredly quite insufficient for the purpose. Thick yellow smoke is copiously evolved at an early stage of the process; but the matter which produces this smoke, and which cannot be inconsiderable in amount, is not represented in the gas of mean composition. It seems, therefore, most probable that the opposite conclusions concerning the amount of hydrogen consumed during the process of coking are due to an error in the average composition of the gases.

TABULAR STATEMENT OF THE PRECEDING CALCULATIONS.

1 part by weight of Coal contains	Combines with	Product of combustion.	Units of heat evolved.	Latent heat to be deducted.	Available units of heat.	
C 0·2368	O of air	CO_2	1913·344	..	1913·344	
H 0·0485 = 0·04479	O of air	HO	1522·860			
0·00371	O of the coal	HO	Nil	234·400	1288·460	
O 0·0297						
N 0·0150	Nil.	Nil	Nil	Nil	Nil	= Units of heat available by the perfect combustion of the carbon and hydrogen existing in one part by weight of coal = 3201·804
Total ... 0·3300				Total	3201·804	
C 0·2368 = 0·1664	O	CO^2	1344·512	Nil	1344·512	
0·0523	O	CO	129·338	Nil	129·338	
0·0181	H	CH^2	Nil.			
H 0·01536 = 0·00603	C					
0·00933	Free.					
				Total...	1473·850	= Units of heat which have been given out by the combustion of the carbon in the oven ...
C 0·0704 = 0·0523	Existing as C O	CO^2	293·2461	..	293·2461	
0·0181	$C H^2$	CO^2	146·2480	..	146·2480	= 2361·349
H 0·01536 = 0·00603		HO	522·240	74·2349	448·0051	
0·00933	H	HO				
				Total...	887·4992	= Units of heat obtainable by the further combustion of the carbonic oxide, marsh gas, and free hydrogen after they have left the oven ....
			Units of heat given out by the hydrogen in the oven			..... = Difference ..... 840·455

Nevertheless it is certain that not only is a large amount of heat developed in the process of coking, but also that a considerable additional amount may be obtained by the combustion of the carbonic oxide, hydrogen, and marsh gas existing in the gases which escape from the ovens. But whether these combustible gases, which are mixed with so large a proportion of carbonic acid and nitrogen, can be *perfectly* burned by atmospheric air, seems to be more than doubtful. Ebelmen draws the practical and obvious conclusion that as a very large proportion of the heat produced in coke-ovens is *sensible* heat, it is desirable that the distance between the ovens and the place of the application of the waste gases escaping from them should be as short as possible. A successful application of these gases to the heating of steam boilers has long been in operation at Seraing; and of the arrangements adopted for the purpose I introduce the following description by Valerius:—

Coke-ovens at Seraing, of which the waste heat and gases are applied to the raising of steam.—A row of eight ovens is built under one boiler, which produces steam sufficient for an engine of eighty horse power. Fig. 40, the elevation; fig. 41, plan of the top; fig. 42, vertical section on the line A B; fig. 43, horizontal section on the line C D; fig. 44, transverse vertical section on the line E F, fig. 43.

The ovens are built of double courses of brick-work, one of fire-brick within, *v*, *v*, and the other of common brick; the floor of fire-bricks is laid flat; H, a chimney in the middle of the oven; *h*, *h*, smaller chimneys at the commencement of the conical part of the roof; the transverse sectional area of the chimney, H, exerts a great influence upon the process of carbonization; it is equal to, or somewhat greater than, the sum of the transverse sectional areas of the two chimneys, *h*, *h*; P, P, doors for charging and drawing; I, I, plates of cast-iron on the level of the ground under each door, in order to receive the coal to be charged, and the coke at the time of drawing; *c*, cast-iron door-frames let into the brick-work; *m*, cast-iron bearers to support the brick-work above the door; L, arched vault, upon which the floor of the oven rests; the vault is intended to protect the oven from the moisture of the ground; *m'*, *m'*, walls which close the ends of the vault; *o*, *o*, holes above the ground by which air may circulate through the vault; *a*, *a*, little channels left in the brick-work between two contiguous ovens, and at the ends of the pile of building on each side of the chimney; they ramify through every part of the brick-work, so as to favour evaporation. As the ovens have to support considerable weight, as well as the strain caused by changes of temperature, they ought to be firmly braced, in order to prevent the brick-work from splitting. The mode of bracing is shown in figs. 40 and 43; in fig. 43, the dotted lines, *b*, *b*, are bars of $\frac{1}{2}$ inch iron, which extend diagonally through the brick-work, and tie firmly together the cast-iron standards, *e*, *e*, and bearer above; these standards are made angular, so as to fit on and protect the free edges of the piers at each entrance of the oven; *b'*, *b'*, ends with screws and nuts of tie-rods of $\frac{3}{4}$ inch iron, which traverse the piers parallel to the long axis of

the oven, and fix the upper bearers above the two opposite doorways of the oven; *a'*, flat tie-bars of iron, three inches broad and half an inch thick, almost wholly enclosed in the brick-work, and intended to hold together the whole pile of building from end to end; there are two such bars on each side, one a little below the level of the ground, and the other a little below the coping of the ovens. The

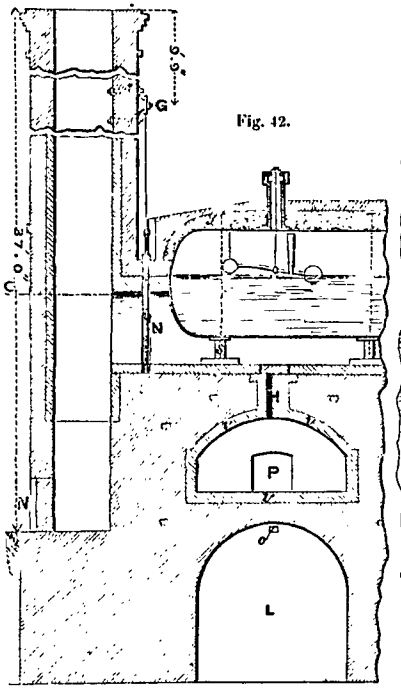

Fig. 42.

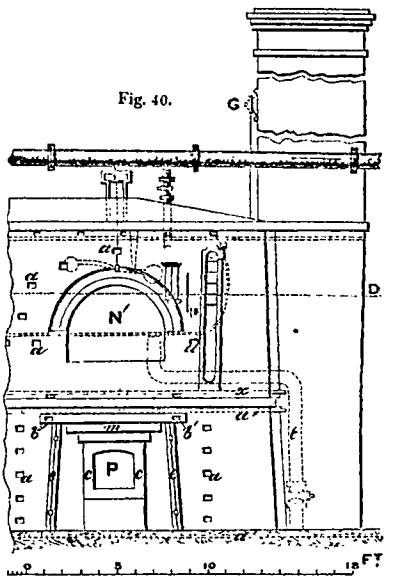

Fig. 40.

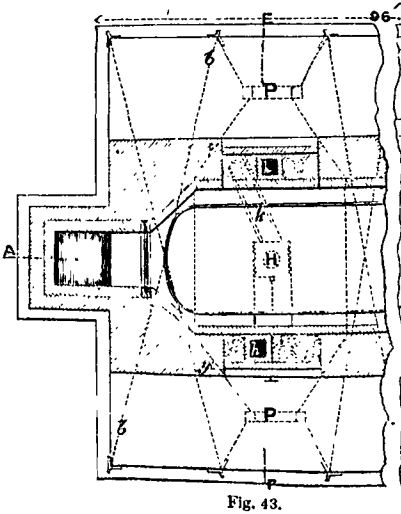

Fig. 43.

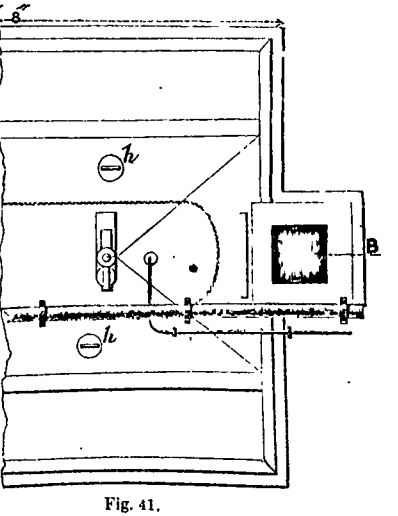

Fig. 41.

door-frame is of cast-iron, and the door, which moves on hinges, consists of a frame of cast-iron filled with fire-bricks; in the upper part of the door is a hole $\frac{3}{4}$ inch in diameter, through which air enters, and the interior of the oven may be inspected. Eight of these ovens are built in a row. At each end is a stack, and from stack to stack extends a long flue, into which open all the central chimneys of the ovens. The stacks are used alternately, so that when one is in communication with the long flue, communication between the other and this flue is cut off by means of the damper, G N; *k*, *k*, fig. 43, channels of cast-iron, terminating upon the floor of the long flue at the openings through which the gases enter from the ovens underneath; these channels convey air necessary for the combustion of the gases; *l*, fig. 44, sliding dampers of fire-brick, which may be moved by iron rods so as to close when necessary the openings which admit the gases.

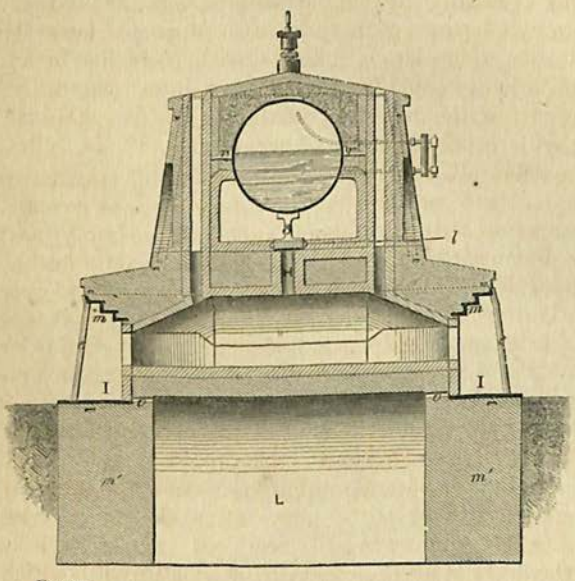

Fig. 44.

When the central chimneys of the ovens are closed by these sliding dampers, as is supposed to be the case in the engravings, carbonization proceeds by means of the lateral chimneys, *h*, which are carried up higher than is required in ovens unconnected with a boiler. That part of these chimneys which is contained within the roof of the oven is cylindrical, while that which rises above the roof is rectangular. In order that the sliding dampers may be worked, it is necessary that the lateral chimneys should not be exactly opposite each other. As these chimneys are not in operation during the process of coking, they are closed at the top by plates of cast-iron, or bricks, around which coke-dust is placed. Corresponding to each door of the oven is an independent arched niche, N'. On the inner side of the brick wall included within this niche, the brick-work is replaced by coke-dust (see fig. 43), through which openings can easily be made in order to examine and repair the boiler. In ovens since constructed coke-dust is not used, and the brick-work within the niche is made solid, with the exception of a doorway on one side of the chimney large enough for a man to pass through. The door is formed of a frame of cast-iron

containing fire-bricks, which fits in like the lid of a tobacco-box, and of which the sides are luted with clay. N, fig. 42, a niche through which a workman may enter each of the main stacks. There are also niches on the sides of each main stack at the end, through which men may get access to the bottom of the boiler. The brick-work of the long flue is provided with vents, *a*, *a*, and is firmly braced together longitudinally by flat iron bars, three inches wide and half an inch thick, and transversely and vertically by similar bars, *y*, figs. 42 and 43. The boiler rests upon cast-iron props, *s*, and is also supported laterally by sixteen pieces of strong iron plate *r*, *r*, fig. 44, each 10 inches broad. The discharging pipe, *t*, is protected from heat by an outer case of fire-bricks. The upper part of the boiler is surrounded with coke-dust, which is covered in with brick-work, as shown in figs. 42, 44. Two rows, of eight ovens each, are built in a line, a space of six metres (about 20 feet) being left between the rows for convenience of passage. A single row of these ovens will raise steam sufficient to supply blast to a furnace of large dimensions, in which coke is used as the fuel.

With a single boiler, 15 feet long and 4½ feet in diameter, fixed over a coke oven in nearly the same manner as shown in fig. 44, it was ascertained. that 146 litres (= 32·13 gallons) of water could be evaporated per hour, under a mean pressure of 2·76 atmospheres, which is equivalent to an average power of 12·41 horses.

As the gases evolved at the commencement of the process of coking contain but little combustible matter and much vapour of water, they are allowed to escape by the lateral chimneys; and the central chimneys are only opened two or three hours after charging. The two main stacks, of which the transverse sectional area of each is equal to the sum of the areas of all the central openings through which the gases pass under the boiler, draw alternately during twelve hours; and the coking is so managed, that every three hours one of the eight ovens ought to be drawn.

The order in which each oven is drawn is indicated by the following diagram:—

Numbers of the Ovens.							
1.	2.	3.	4.	5.	6.	7.	8.
During the Day.				During the Night.			
Hour of the Clock.				Hour of the Clock.			
3.	12.	9.	6.	6.	9.	12.	3.

Three advantages are thus obtained:—as the boiler throughout its entire length receives equal amounts of heat, the wear is uniform;—the combustion of the gases is secured, as the gases of the ovens in full activity pass over the openings of those less advanced;—the intermitting action, which is due to the irregularity in the progress of each oven taken separately, disappears, because the gases of the ovens in different stages of advancement become mixed, so as to produce a uniform effect. This last object, it is stated, is attained to perfection, as the index of the steam gauge remains stationary to a degree which would be difficult to obtain by ordinary methods of heating. When

three rows of ovens, containing eight each, are employed, the numbers annexed indicate the order in which the charging and drawing take place, the twenty-four hours of the day being represented by the numbers from 1 to 24 consecutively :—

First Row.	Second Row.	Third Row.
4. 1. 7. 22. 10. 19. 13. 16.	5. 2. 8. 23. 11. 20. 14. 17.	6. 3. 9. 24. 12. 21. 15. 18.

Valerius states that the following practical results are obtained by the combustion of the gases and waste heat of three rows of ovens, containing eight each. Over each row a boiler is fixed in the manner described. The combustion of the gases from thirteen ovens takes place at the same time, while the remaining ovens only contribute to the result by yielding sensible heat. Sufficient steam is raised for a condensing blowing engine, which works expansively at an average pressure, and supplies blast to two large furnaces, in which coke is the fuel used, and for a small steam-engine of 10-horse power, which raises the charges on an inclined plane to the tunnel heads of these furnaces. The diameter of the blowing cylinder is $7\frac{1}{2}$ feet, the length of the stroke 8 feet, the number of revolutions per minute is 10, and the pressure of the blast is $3\frac{3}{4}$ lbs. on the square inch; results which, according to calculation, require 117-horse power. The saving of fuel thus effected is estimated at 9360 kilogrammes of coal daily, or, in round numbers, between 9 and 10 tons.

Davis's Breeze-oven.—A patent was obtained for this oven in 1856 by Mr. Joseph Davis, of Birmingham, under the title of "a new or improved method of manufacturing the small coke, commonly called breezes, which said method of manufacture economises heat, and effects the suppression or partial suppression of smoke."[9] Many of these ovens are in operation in Birmingham and the vicinity. I inspected one in 1860 at the Swan Foundry, Oldbury, belonging to Messrs. Taylor and Ensor, to whom I am indebted for the drawings from which the annexed woodcuts were made. Fig. 45, front elevation; fig. 46, horizontal section on the line AB, fig. 45; fig. 47, vertical section on the line CD, fig. 46.

The oven consists of a chamber lined with fire-brick; the side walls are vertical, and gradually approximate towards the opening in front; the wall at the back is also vertical; the roof is arched; the floor is flat, except the sloping part in front, and in it is a grate, *a*, below which is an ash-pit, *b*, provided with a cast-iron door, *c*; the front is closed by the cast-iron doors *d d* and *e*. At the upper part of the side wall on the left are two openings, *g g*, communicating with the contiguous fire-place, F, from which the flame passes through the tubes G G of a steam-engine boiler. There is a cistern, *k*, filled with water, which may be conveyed through the iron pipe *h*, and injected into the oven from a series of holes in the movable transverse pipe *i*. The non-caking "thick coal" slack of Staffordshire is employed in this oven. The slack is screened, and the finer part is burnt on the grate

[9] Specification, A.D. 1856. No. 1424.

adjoining the boiler, while the remainder is converted into "breezes" in the oven above described. The process is conducted as follows: Fire is lighted on the grate of the oven, the ash-pit door being open and the doors above closed; and when a considerable mass of incandescent fuel has accumulated, the ash-pit door is closed, and continues so until the end of the operation. Slack is then thrown into the oven, and spread as evenly as possible. A copious evolution of inflammable gas is produced, which takes fire, and continues to burn by means of the air which finds its way through crevices around the sides of the doors in front. When the coal last thrown in has yielded its gas, and flame ceased to be evolved in a sensible degree, a fresh supply is introduced, and so on at intervals until the oven has become filled as far as practicable. The coke is then extinguished by injecting water into the oven through the uppermost door in front, after which it is immediately withdrawn through the middle door. During this period it is necessary to burn some of the larger slack on the adjoining grate, in order to keep up the steam. The "breeze" which I saw thus produced had a brilliant silvery lustre. Mr. Ensor informed me that in one week this oven will produce from an amount of slack costing 30 shillings, "breeze" of the value of from 50 to 55 shillings. The "breeze" is in great request for smiths' fires. The patentee undertakes to erect an oven like that described for the sum of 50*l.*, and to make no further claim for the use of his process.

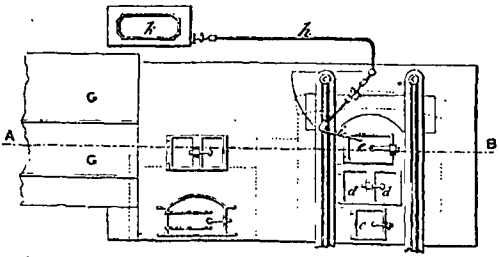

Fig. 45.

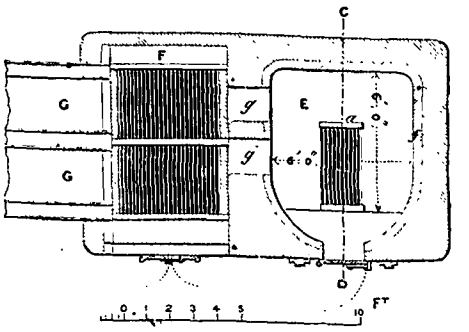

Fig 46.

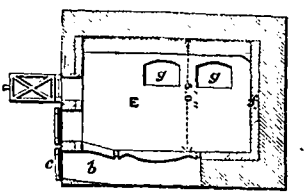

Fig.

In 1847 a patent was granted to G. A. Michaut for the "production and application of heat, and manufacture of coke," which appears to me very closely to resemble, if it be not identical with, that of Mr. Davis.[1]

[1] Specification, A.D. 1847. No. 11,997.

Mineral charcoal.—At the Great Exhibition of 1851, Mr. Rogers, of Abercarn, exhibited a specimen of what he termed *charred coal*, but which he now designates *mineral charcoal*. It is a light, porous, almost pumice-like coke, which he recommends as a substitute for wood charcoal in the manufacture of tin-plate.

At the time mentioned above, Mr. Rogers refused to divulge the process of its preparation; but in 1858 he published the following account of it at a meeting of the South Wales Institute of Engineers. The coal is first reduced to "small," and washed by any of the ordinary means; it is then spread in its wet state over the bottom of a reverberatory furnace to the depth of about four inches, the bottom of the furnace having been previously heated to redness. When the coal is thrown in, much gas is evolved, and great ebullition occurs. A light spongy mass is thus produced, which is turned over in the furnace, and drawn in about an hour and a half. Water is then freely sprinkled over the mass until the smell of sulphuretted hydrogen ceases. In preparing mineral charcoal he has availed himself of the floor of an ordinary coke-oven immediately after the charge has been drawn, and while it was still red-hot.[2] A short time after the preceding description was published, Mr. Thomas read a paper to the same Institute on the manufacture of iron with *mineral charcoal*. After preparing and working a large quantity of this *new fuel*, he makes the rather startling announcement, "that it makes much better iron, for the manufacture of tin-plate, than that produced from the puddling process, or where wood charcoal is employed as a refining fuel."[3] He further states, "the iron made from the finer's lump, and after rolling, differs in no respect from iron made with wood charcoal; it is quite as strong and very clean." As much work may be done with five shillings' worth of mineral charcoal as with twenty-four shillings' worth of wood charcoal. The mineral charcoal which Mr. Thomas, formerly blast-furnace manager at the Pontypool Iron-Works, used in his experiments was produced from a seam of coal locally termed the *wing*, which has always been celebrated for its superior quality as an iron-making coal. The following analysis of this coal was made by Mr. W. Ratcliffe in Mr. Rogers's laboratory.

Composition of the Coal.		Composition of the Ash.	
Carbon	81·13	Silica	25·32
Hydrogen	4·72	Alumina	33·45
Nitrogen	1·03	Sesquioxide of iron	11·39
Oxygen	10·12	Lime	16·06
Sulphur	traces	Magnesia	6·60
Ash	3·00	Potash	0·96
		Soda	trace
	100·00	Sulphuric acid	4·81
		Phosphoric acid	0·81
		Loss	0·60
			100·00

After a week's trial Mr. Thomas found the yield of mineral char-

[2] Proceedings of the South Wales Institute of Engineers, Merthyr Tydvil, Jan. 1858, v. 1, p. 19.

[3] Ibid. v. 1, p. 101, April, 1858.

coal from this coal to be nearly 78·3 per cent.; whereas coal from the same seam, when subjected to the ordinary process of coking in ovens during forty-eight hours, yielded about 64 per cent. It is to be regretted that an analysis of the mineral charcoal has not been published; for without a knowledge of its composition the figures of Mr. Thomas just cited lose much of their value. Mr. Rogers, in announcing the preparation of mineral charcoal as a novel invention in 1851, could not have been aware of the fact that a process identical with that which he has described for its preparation had certainly been published in this country in 1826, and again in 1841, as will appear from the following extract:—

"When coke is required to be more of the nature of charcoal, the process is conducted in a different manner. The small coal is then thrown into a large receptacle, similar to a baker's oven, previously brought to a red heat. Here the door is kept constantly open, because the heat of the oven is of itself sufficient to dissipate all the bitumen of the coals, the disengagement of which is promoted by frequently stirring the coal with a long iron rake. The coke from these ovens, though made with the same kind of coal, is very different from that produced by the former operation (*i. e.* as practised in ovens of the Duke of Norfolk's colliery, described at p. 157); this being intensely black, very porous, and as light as pumice-stone."[4]

Coking of non-caking coal slack by admixture with pitch.[5]—In 1854 Mr. John Bethell obtained a patent for the manufacture of coke by heating pitch, or pitch mixed with coal. Coal-tar pitch is preferred on account of its cheapness. It is broken into small pieces, and well mixed with the coal in the proportion of 1 ton to 4 tons of coal, and the mixture is converted into coke by burning it either in coke-ovens or in piles. In the provisional specification no claim is made in reference to the agglomeration of coke-dust or small pieces of coke by this process; whereas in the specification itself such a claim is entered. Several years before the date of this patent I had employed with complete success gas-tar in admixture with anthracite powder, or the powder of gas-retort carbon, in the preparation of carbon crucibles of large size. In 1858 Mr. Bethell procured a second patent for making large coke of good quality, by heating in a common coke-oven a mixture of breeze (dust or very small coke, of which large quantities may be obtained at a low price at gas-works) and coal-tar, or coal-tar pitch. As this invention is claimed in the specification of the first patent—except the use of coal-tar—the reason of its introduction into that of the second patent is not very obvious. In 1859 I had the opportunity of witnessing Bethell's process in operation at Llanelly, South Wales. The mixture employed consisted of crushed anthracite

[4] Parkes's Chemical Catechism, 1826, p. 451. This description was again published nearly verbatim in the History and Description of Fossil Fuel, the Collieries, and the Coal Trade of Great Britain. By the Author of the 'Treatise on Manufactures in Metal' in the Cabinet Cyclopædia. 2nd ed., London, 1841, p. 413.

[5] This patent has expired from non-payment of the fees which became due some time after it was granted.

and coal-tar pitch. The anthracite was previously washed. The men appeared to suffer much from irritation of the eyes and skin, especially about the face, caused by the fine particles of pitch. Bethell's process has been re-patented more than once; and if persons will thus squander their money in spite of the marvellous facilities which, thanks to my friend Mr. Bennett Woodcroft, now exist for obtaining gratuitous information on the subject of patents, they have chiefly themselves to blame. In 1857 Mr. William Cory obtained a patent for the manufacture of coke by heating the slack of free burning coals and anthracite with gas-tar or pitch, of which, if the mixture is intimate, the proportion of one-fifth or one-tenth of the weight of the coal will suffice.[6] At the end of the same year Bethell's process was again patented by Carl Buhring, who, in addition to pitch, claimed the use of asphalt, sugar, wax, or any other bitumen, rosin, or gum, or any mixture of these materials. The claim, as is usual in such cases, is made as comprehensive as possible, and embraces "carbonized animal or vegetable materials," "such as coke, charcoal, boghead ash, peat coal, wood, bone, dried blood, peat, or any such material which by the action of heat may be carbonized."[7] During the last nine years, in the Metallurgical Laboratory of the School of Mines, in lining crucibles we have employed lamp-black and charcoal mixed with treacle and starch, substances which appear to have eluded the grasp of this patentee.

In 1858 a provisional specification was filed by Mr. J. T. Smith for "the manufacture of coke from small coal, or the small coal called breezes," by admixture with tar, or tar deprived of its naphtha, or a portion of its oil. This gentleman acted wisely in not proceeding further with his application.[8]

In 1860 Mr. Jabez Church obtained a patent for Bethell's process, with the addition of lime or carbonate of lime in the proportion of 25 lbs. of slaked lime to 140 lbs. of asphalt, or pitch of coal-tar, and 1 ton of coal. He also claims the use of coke, breezes, or cinders, ground or unground, except that he first washes these substances "to take out the sulphur compounds of iron, and other impurities which they may contain."[9] The patentee may be assured that his title to the exclusive right of this washing process with the object declared is not likely to be disputed, at least by persons possessing an elementary knowledge of chemistry. For what reason lime is employed we are not informed. However, a patent had been previously obtained by Dr. Hermann Bleibtreu in 1857 for the manufacture of coke for metallurgical purposes, from small or crushed coal in admixture with powdered limestone, chalk, burnt lime, or other calcareous substance. The object of the invention is stated to be "to prevent the impurities of coal, such as sulphur, silica, alumina, phosphorus, &c., from exercising an injurious influence upon the products of metallurgical processes."[1] This lime coke, it is stated, is applicable to all purposes for

[6] Specification, A.D. 1857. No. 1174.
[7] Ibid., No. 3194.
[8] Ibid., A.D. 1858. No. 1614.
[9] Ibid., A.D. 1860. No. 784.
[1] Ibid., A.D. 1857. No. 1528.

which common coke may be used; "but it will be found most valuable for the manufacture of iron and steel, and will be the means of producing a quality of iron far superior to that produced by the use of coal or common coke," or perhaps nearly if not quite equal to charcoal iron." How far these advantages are likely to be realized will be discussed in a subsequent part of this work. Mr. Jabez Church, acting on the principle of killing two birds with one stone, has combined in his single patent the two processes previously patented by Bethell and Bleibtreu.

In 1850 Mr. James Palmer Budd, of Ystalyfera, near Swansea, obtained a patent for the manufacture of coke by heating non-caking coal in intimate admixture with caking coal, the more strongly caking the better. The two kinds of coal may be ground together in a pug-mill, similar to that used for grinding mortar, or rolls may be employed for the purpose, either with or without grooves. It is not so important to crush the lumps of the caking coal as those of the non-caking coal. No particular method of coking is claimed; nor are definite quantities of the two kinds of coal prescribed, as the proportion of caking coal will necessarily depend on the degree of its caking quality. It is, however, recommended that in the first instance trial should be made of a mixture of equal weights of the two kinds of coal; and if a sound coke be not thus obtained, the proportion of caking coal must be increased until coke of suitable quality is produced. Every variety of non-caking coal, inclusive of anthracite, is suitable for this process.[2] In 1856 Mr. Budd's process was again patented not less than three times—the first time by A. Perpigna;[3] the second time by Mr. R. A. Brooman, who asserts that the distinctive feature of his invention is "to reduce the materials to a powder before mixing them, instead of first combining them and then reducing them to powder;"[4] and the third time by Mr. L. S. Magnus.

In 1858 a provisional specification of the same process was filed by Messrs. Yelverton and Bowen, who proceeded no further in the matter, and prudently retained the money which otherwise would have been expended in vain.

Collection of products of economic value generated during the process of coking.—Long anterior to Murdoch's great invention of lighting by coal-gas, experiments had been made by various chemists on the nature of the products of the destructive distillation of coal. Early in the last century Hales communicated to the Royal Society the fact that half a cubic inch or 158 grains of Newcastle coal yielded in distillation 180 cubic inches of air.[5] Neumann states that "48 ounces of pit-coal distilled in a glass retort, with a fire gradually increased, yielded 2 ounces 7 drachms of phlegm, 2 ounces and 1 drachm of a thin fluid oil, and 1 ounce of a thick, tenacious, ponderous, pitchy oil, which stuck in the neck of the retort; the residuum weighed 42 ounces 7 drachms. The distilled liquors gave marks rather of an

[2] Specification, A.D. 1850. No. 13,121.
[3] Ibid., A.D. 1856. No. 873.
[4] Ibid., No. 1828.
[5] Statical Essays, 1, p. 182, 3rd ed. 1738.

urinous and ammoniacal character, changing syrup of violets greenish, and emitting an urinous odour on the admixture of fixed alkaline salts or quick-lime. The oil arose in yellow fumes, and smelled considerably sulphureous; it somewhat stained polished silver, but the stains were easily rubbed off. That which distilled at first was light, and swum on water; the succeeding parcels proved more and more gross and ponderous, and at last sunk."[6]

Genssane, in 1770, published a detailed and interesting account of the mode in which pit-coal was distilled at iron-works at Sulzbach. His description was founded on personal observation. The distillatory apparatus consisted of a chamber or large muffle of refractory clay, heated by a fire-place on each side. There were two openings in front provided with doors, an upper one through which the coal was charged, and a lower one through which the coke was withdrawn. The sides of the chamber were vertical, and the roof was arched. The bed was flat, and sloped downwards towards the back, in the bottom of which was a pipe communicating with a receiver on the outside. In this pipe was fixed another vertical pipe for the exit of the uncondensable products. There were not less than nine of these furnaces built together in a row, and at least three were in operation, while three others were cooling. When the coal was half-coked in the first three, the other three were lighted, and so on in succession. As the coking generally lasted three days, the coke was withdrawn daily from three furnaces, and three others were charged. The coal lost in coking an eighth of its weight.

The charge for each furnace was about a ton of raw coal, and somewhat less than half this weight of coal was required to distil a charge. The coke was used to smelt iron. Genssane makes the following remarks:—"Coal thus cooked (cuit) exhales not the slightest odour in burning; and it has the advantage of lasting twice as long in the fire as wood-charcoal, instead of which it may be used for all purposes without fear of the least inconvenience. Let us reflect now on the importance of this discovery, especially in France, where wood and charcoal have become so scarce. This is not all: the oils and bitumens obtained in this operation almost pay the expenses of it. These two matters are thus turned to account. They collect together in the great receiver; the mixture is poured into a large tub, and stirred during a long time with wooden instruments worked by hand; by this manipulation the oil collects on the top, and is taken off with iron spoons, while the bitumen falls to the bottom of the tub;[7] this is sometimes sufficiently pure to be at once sent into the market; but more frequently it is surcharged with water; it is then boiled in a copper until the water is evaporated, and it deposits a cottony matter, which is thrown away. After this the pure bitumen becomes very greasy

[6] The Chemical Works of Caspar Neumann, M.D., abridged and methodized by William Lewis, M.B. London, 1759, p. 245.

[7] According to Mansfield the specific gravity of coal-tar varies from about 1·120 to 1·150; the lightest samples containing the largest proportion of fluid oils. Quarterly Journ. of the Chemical Society of London, 1849, 1, p. 249.

and liquid, and is in no respect inferior to the best grease for carriages. There is no difference between this oil of coal and that distilled from petroleum, except that the latter is much more inflammable and suddenly catches fire; and it may be usefully employed in lamps by people in the country. No other light is used in the mines of Sulzbach; but it smokes much, and exhales a tolerably strong smell of bitumen."[8]

The manufacture of oil for lamps and for the purpose of lubrication, by the distillation, at a low temperature, of cannel coal and other bituminous matters, is now conducted on a large scale in this country, and is reported to yield a princely income to the manufacturers, Messrs. Young and Company. The oil thus produced contains paraffine, and is accordingly designated paraffine oil by Mr. Young, who obtained a patent for his invention in 1850.[9] Although the oils used at Sulzbach were probably dissimilar from paraffine oil, yet it is not a little singular that products obtained so long ago from the distillation of coal should have been employed as agents of illumination and lubrication, just as other products also derived from the distillation of coal are now applied to the same purposes.

The history of the process of coking at the iron-works at Sulzbach is interesting in another point of view, as showing how completely a great practical discovery may obtrude itself, as it were, upon the attention of men, and yet be unperceived. The chamber in which the coal was distilled was essentially a gas-retort; and the gas, which issued in a continuous current from the vertical pipe at the back, must often have taken fire and produced a luminous flame; but the idea of applying that gas to the purpose of lighting seems never to have occurred to those who observed it. Large gas-works were daily in active operation at Sulzbach, and yet the merit of the invention of lighting by coal gas was reserved for Mr. Murdoch in 1792, or more than twenty years afterwards.

In 1781 the Earl of Dundonald obtained a patent "for the extracting of tar, pitch, essential oils, volatile alkalies, mineral acids, and salts, and the making of cinders (coke) from pit coal," by the heat of combustion developed *within* the distillatory vessel, and not on the *outside*, as, he asserts, had always previously been the practice. A regulated supply of external air was admitted into the interior of the "vessel or building" containing the coals to be distilled, "by which means the said coals after being kindled are enabled, by their own heat and without the assistance of any other fire, to throw off in distillation, &c." It was this particular mode of conducting the process which he claims as his invention, and if the claim were correct, to the Earl of Dundonald we should be indebted for the principle of the present system of coking in ovens; but it is evident from Horne's description, published in 1773, and previously inserted at p. 145, that coking was then conducted on exactly the same principle. The specification of this patent contains the following interesting passage,

[8] Traité de la Fonte des Mines par le feu du charbon de terre, etc. Par M. de Genssane. Paris, 1770, 1, p. 265 et seq.

[9] Specification, A.D. 1850. No. 13,292.

from which we may infer that the Earl knew that several matters were produced by the distillation of coal, which possessed different degrees of condensability:—

"Exclusive of the above invention, for which only the patent has been obtained, I promote the condensation of the loss coercible part of the vapour that comes off in distillation by commixing it with the steam of boiling water, and complete the condensation by the means of cold water. . . . I also cause the vapour to pass through more condensing vessels than one, to separate by that means the different oils and substances according to the different degrees of cold and moisture requisite to condense."[1]

In 1852 a patent was granted to Mr. W. E. Newton for "the adaptation to ordinary coke ovens of an apparatus whereby the gaseous products evolved during the combustion of coal therein may, without interfering with the ordinary process of coking, be drawn off and conveyed away to a receptacle or chamber where they may be separated from each other, and combined with other chemical agents to form valuable products, or used for some other useful purpose."[2] Ammoniacal compounds are specially mentioned amongst the condensable products; and the residual combustible gases are conducted under steam-boilers or any other apparatus, and there burned by the admission of atmospheric air.

In 1859 the late Mr. Edward Jones, of the Russell's Hall Ironworks, near Dudley, obtained a patent for collecting and condensing mainly or wholly the tar or other condensable volatile products given off during the process of coking in open fires or heaps.[3] I visited these works in 1860, and saw the process of condensation in operation. The fires were constructed in the usual manner with a central chimney, as described at p. 149. The bottom of the chimney was connected with an underground flue, which communicated with an old steam-boiler containing coke, and having a tap at the bottom; and the boiler, in its turn, communicated with a stack. A series of coke-fires were put in connection with the underground flue. Before or soon after igniting the coke heap, the top of the central chimney is closed by a damper. The volatile products then pass downwards through the underground flue, and such as are condensable accumulate in the boiler, from which they are drawn off by the tap at the bottom. A considerable quantity of tar and other matters were thus obtained. I was informed that in regard to the yield and quality of coke, Mr. Jones's process was not inferior to the ordinary method.

Desulphurization of Coke.—When coal is exposed to a red heat, the bisulphide of iron or pyrites which it contains is reduced to protosulphide, and, accordingly, this sulphide is present in coke. The sulphurous acid evolved from burning coke is due to oxidation of the sulphide by the oxygen of the atmosphere; and the escape of sulphuretted hydrogen occasioned by the action of water on incandescent

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[1] Specification, A.D. 1781. No. 1291. [2] Ibid., A.D. 1852. No. 13,974.
[3] Ibid., A.D. 1859. No. 2158.

coke is caused by the same sulphide, which at a high temperature decomposes water, with the liberation of that gas and the formation of oxide of iron. In certain metallurgical operations in which coke is employed as fuel, the presence of sulphide of iron in sensible quantity may produce very injurious effects. Iron pyrites is frequently so intimately mixed with coal that it is impossible to separate it by mechanical means; but, were it possible to do so, it would be necessary in the first instance to crush the coal to powder, so that only caking coal could be operated upon; unless, in the case of non-caking coal like that of South Staffordshire, recourse were had to the process of mixing with pitch or some other similar matter. There is no practical method known at present by which the powder of this coal can otherwise be made to cohere by coking.

An impression has long prevailed that when red-hot coke is extinguished with water it loses a considerable amount of sulphur, and is thereby improved in quality. Scheerer has published the following result of an experiment made to determine the proportion of sulphur which may be eliminated from coke by the action of a current of steam.[4] High-pressure steam was passed into a coke oven containing red-hot coke, ready to be drawn; but, previously, some of the coke was taken out for analysis, and found to contain 0·71 per cent. of sulphur. The coke, after having been during some time exposed to the action of steam, was found to retain 0·28 per cent. of sulphur; so that a reduction in the quantity of sulphur from 1·0 to 0·4 had occurred. Many years previously Nordenskiöld introduced the practice of desulphurizing iron ores containing sulphide of iron, by subjecting them at a red heat to the action of steam.

The application of steam to the desulphurization of coke has been patented in this country by Messrs. Claridge and Roper.[5] They employ a coke-oven, having a false perforated bottom, underneath which, at any time during the process of coking, steam can be admitted and made to ascend through the stratum of coke above. In an oven of the same construction they also propose to introduce through the bottom, in aid of the process of coking, the waste gases of iron-smelting furnaces.

It must be borne in mind that when steam is passed through red-hot coke, it is decomposed with the production of hydrogen and marsh gas, carbonic oxide, and carbonic acid. I am indebted to Dr. Frankland for the following analysis of the gaseous mixture resulting from the action of steam on red-hot Derbyshire coke:—

Hydrogen and marsh gas	56·9
Carbonic oxide	29·3
Carbonic acid	13·8
	100·0

Hence it will appear that a sensible amount of carbon may be carried away, if the exposure of the coke to steam be long continued.

[4] Berg. u. Hüttenm. Zeit. 13, p. 239. 1854.
[5] Mr. Roper was a student at our School of Mines.

When we reflect upon the physical state of coke, especially of that which is compact and comparatively free from porosity, it is difficult to conceive how there should be extensive contact between the steam and the sulphide of iron, which, to a considerable extent, must be enclosed in the substance of the coke. In the case of light and very porous cokes this contact would exist in a greater degree, yet it would nevertheless be far from sufficient to effect perfect desulphurization.

Mr. Calvert, of Manchester, has patented a method of desulphurizing coke by means of common salt, the principle of which he explains as follows:—"By the action of heat, bisulphide of iron is decomposed into protosulphide, which, in contact with chloride of sodium, forms, amongst other products, chloride of iron, which, in the presence of the vapour of water at a high temperature, is resolved into oxide of iron and hydrochloric acid."[6]

Mr. Calvert has published the results of numerous experiments which would appear to lead to the conclusion that cast-iron melted in cupolas with *salted coke* contains less sulphur than when melted with ordinary coke. These results are not, in my judgment, conclusive. To determine the desulphurizing effect ascribed to salt in a satisfactory manner, a given variety of coal should be coked with and without the salting process, and the sulphur retained in the coke in each case should be exactly determined. I wrote to Mr. Calvert to ascertain whether he had made experiments of this kind, and in reply he communicated to me the following comparative results:—Coke prepared without salting from a coal occurring in North Staffordshire contained 2·56 per cent. of sulphur; whereas salted coke from the same coal contained only 0·72 per cent. But it would not be safe to rely on the results of this single experiment; and I am rather surprised that, as Mr. Calvert attaches much importance to his process, he should not have sought to establish it on unquestionable data.

Cost of coking.—1. At the Dowlais Iron-works, Merthyr Tydvil (November, 1860). The information has been kindly supplied by Mr. Menelaus, the manager, with the consent of the trustees by whom this large establishment is now carried on. The ovens are simple arched rectangular chambers, of the ordinary construction, in which air enters through the top of the door in front, and the volatile products escape into a stack at the back provided with a damper. They are 13 feet long, 6 feet wide, and 4 feet 6 inches high from the floor to the top of the arch. The thickness of coal when charged is about 27 inches, the quantity of coke drawn is 50 cwts., and the time of coking 48 hours. The coal from which coke for the blast-furnaces is made consists of a mixture of caking coal from the Troedyrhiw or uppermost seam, with from $\frac{1}{5}$ to $\frac{1}{4}$ of small semi-bituminous blast-furnace coal. From 25 to 26 cwts. of coal produce 1 ton of coke. The cost of labour for simply coking, that is, filling the oven, tending

[6] Comptes Rendus, 35, Sept. 27, 1852. Date of the patent A.D. 1851, Oct. 30, No. 13,793.

the burning, and drawing, amounts to $7\frac{7}{10}d.$ per ton. At one batch of 60 ovens a small steam-engine is employed for drawing the coke from the ovens; this saves 1*d.* per ton in labour, which is thus reduced to $6\frac{7}{10}d.$ per ton. There are the extraneous charges of filling the coke and horsing it to the furnaces, which raise the cost of labour on the coke when delivered at the furnaces to 1*s.* 2*d.* per ton. The cost, per ton of coke, of bricks and clay is from $\frac{5}{10}d.$ to $\frac{6}{10}d.$, and of castings, bar-iron, and stores $1\frac{1}{2}d.$ The total costs, per ton of coke, inclusive of labour, are as follows:—

	s.	*d.*
Coking	0	$6\frac{6}{10}$
Extraneous labour and hauling to the furnaces	0	$7\frac{1}{10}$
Castings, bar-iron, and stores	0	$1\frac{5}{10}$
Bricks and clay	0	$0\frac{6}{10}$
	1	$4\frac{1}{10}$

The coke is not cooled by watering in the ovens, and this accounts for the small charges for bricks and repairs.

2. In Cox's ovens at the Ebbw Vale Iron-works, Monmouthshire. I am indebted to Mr. Adams, the manager, for the following information. A description and engravings of these ovens have been given at p. 159. The cost of the ovens is from 75*l.* to 80*l.* each. The cost of repairs is 3*d.* per ton of coke. The cost of coking (November, 1860) is 1*s.* 5*d.* per ton of coke, statute weight of 2240 lbs.; but this has been reduced to 1*s.* 1*d.* per ton (June, 1861). Mr. Cox, the inventor of the ovens, conducts the process of coking by contract, and finds all the labour, the Ebbw Vale Company supplying bricks, clay, and iron. All the coals at Ebbw Vale are coked. The yield of coke is 70 per cent. of the weight of the coal; and when the ovens are in good order and making *best* coke, it is as much as 72 per cent. The coke is cooled by watering in the ovens. The water retained in the coke, according to Mr. Parry's determination, is under 1 per cent. The weight of a cubic foot of coke deduced from the weight of a truck filled with coke and containing $171\frac{1}{2}$ cubic feet was 29 lbs.; and in a similar determination with a truck containing $256\frac{3}{4}$ cubic feet, it was found to be 32 lbs.

3. At the Blaina and Cwm Celyn Iron-works, Monmouthshire. Mr. Levick has kindly furnished me with the following information (November, 1860). At the Blaina works in outdoor coking in long ridges, or, as they are termed, "pits," the cost is $7\frac{1}{2}d.$ per ton of pig-iron made. It is a practice in some works thus to contract with the coker on the iron made. For sale-cokes the cost by the same process is $6\frac{1}{2}d.$ per ton of coke. At the Cwm Celyn works the cost of coking in Cox's and other ovens is $6\frac{1}{2}d.$ per ton of coke on the ton of pig-iron made. Mr. Levick, at my request, was so good as to have the following determinations made:—

	Ton.	cwt.	qr.
The weight of Elled coal in two of Cox's ovens amounted to	4	13	0
It measured $8\frac{1}{4}$ cubic yards.			
The coke produced weighed	4	0	0
It measured, after having been broken in pieces, $10\frac{3}{4}$ cubic yards.			

The coke after having been drawn was heavily watered, and was found to retain 16 per cent. of water.

The percentage of coke produced was	86
Deduct water	16
Percentage of dry coke	70

In measuring the coal and coke a box 3 feet square and 18 inches deep was employed; and the measurement was "strike" measure, a portion of small coal or coke being used to level the top.

Combustible Gases.

Carbonic oxide.—The gases which escape from the tops of blast-furnaces, such as are used for smelting iron, &c., contain a large proportion of carbonic oxide, which may be conveyed through pipes to a distance, and employed as fuel under steam-boilers, and for other purposes. The condition under which this gas is formed by the action of atmospheric air on carbonaceous fuel heated to bright redness has been previously explained; and this condition is necessarily present in blast-furnaces. The methods by which the gases of these furnaces, or, as they are termed, "waste-gases," are utilized on the Continent and in this country will be hereafter fully considered under the subject of Iron. But furnaces are now expressly constructed for the

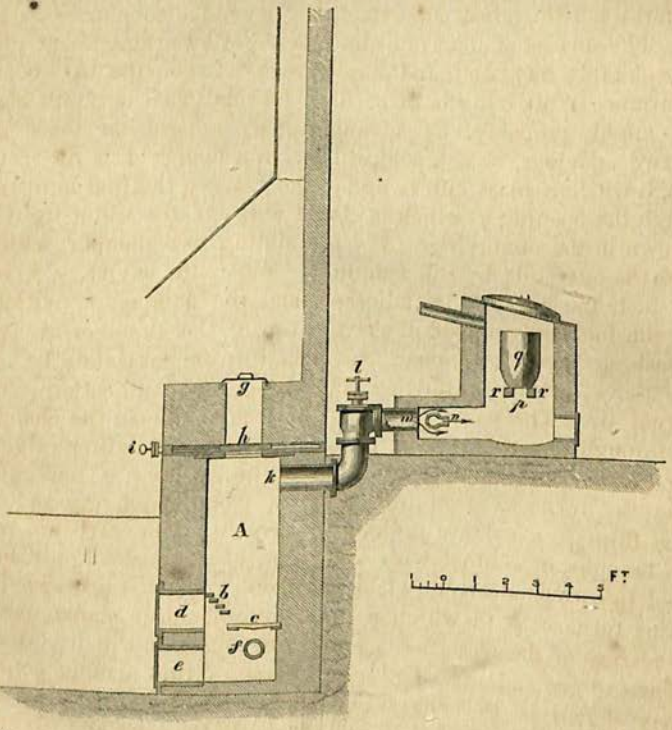


Fig. 48.

generation of carbonic oxide, to be applied as fuel in various metallurgical operations, and it is very important that practical British metallurgists should be made acquainted with their construction, as it seems probable that they may be adopted with advantage in this country. Under the present head I shall describe two furnaces of this kind by way of illustration.

The first of these furnaces is in use in the Mint and the Royal Porcelain Manufactory at Berlin. I am indebted to Dr. H. Wedding of that city for the following description of it, and the drawing from which the accompanying woodcut has been executed. The furnace was made in the foundry of his brother, Mr. W. Wedding, of Berlin, so that all the details may be relied upon as accurate. Brown coal has been employed with perfect success in this furnace, but a better result is now obtained with bituminous coal, which produces less ashes. The engraving represents a vertical section through the middle. A is a chamber of fire-brick, having an ordinary flat grate composed of bars, *c*, and another grate above, in which flat bars of iron are placed crosswise one above another, like steps, *b*. The last kind of grate is called Treppenröst, or step-grate, by the Germans. The bars should be flat, horizontal, and comparatively broad. On a grate of this kind small free-burning coal may be consumed, which would in great measure drop through an ordinary grate. The distance between the bars should be such that the small coal, in dropping from one to another, may form a little talus, not extending beyond the outer edge of the bars. The surface of the grate, by this step-like arrangement of bars, is considerably increased, and ample space between the bars is left for the entrance of air into the furnace. The small coal of South Staffordshire might, probably, be advantageously burned on these grates. The two openings, *d*, *e*, are closed by iron doors; *f* is an iron pipe through which a blast enters under the grates; the fuel is introduced through the opening *g*, which is closed with an iron water-tight cover, as shown in the engraving. At *h* is a sliding iron damper, which may be drawn outwards by the handle, *i*. When the cavity, *g*, *h*, is filled with fuel, the cover, *g*, is adjusted, and the damper, *h*, withdrawn: after the fuel has dropped down, the top of the chamber, A, is closed by pushing back the damper, *h*. The furnace may thus be charged from above, without allowing any direct communication with the external air. The gases generated by combustion in the chamber, A, pass through the iron pipe, *k*, provided with a regulating valve, *l*, and escape at *m*. Immediately in front of the opening, *m*, and extending across the furnace, is an iron pipe, *n*, from which atmospheric air issues through a narrow projecting piece, *n*. The carbonic oxide is thus brought in contact with a stratum of atmospheric air, and converted into carbonic acid, when the flame produced proceeds into the melting furnace, *p*, in which a large crucible, *q*, is shown resting on two bearers of fire-clay, *r*, *r*. The arrows indicate the direction of the currents of gas and air. The other parts of this arrangement are so clearly shown in the engraving, that further description would be superfluous. In order to represent both the gas and the melting

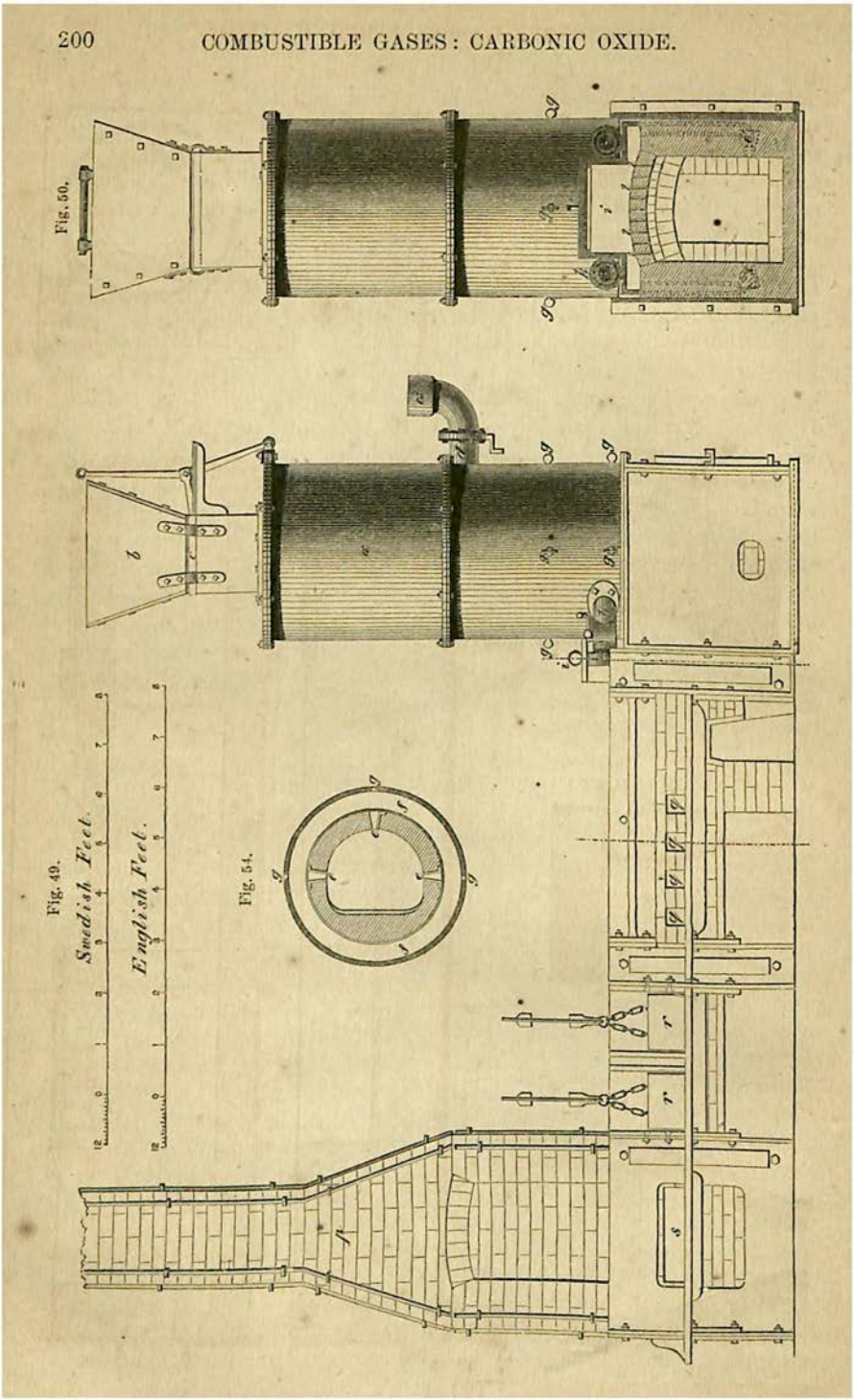


Fig. 50.
Fig. 49.
Swedish Feet.
English Feet.
Fig. 54.

Fig. 55.

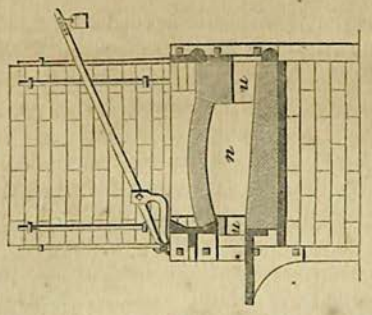


Fig. 53.

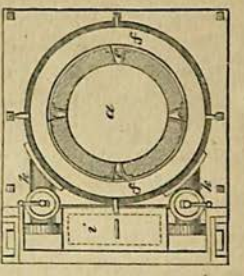
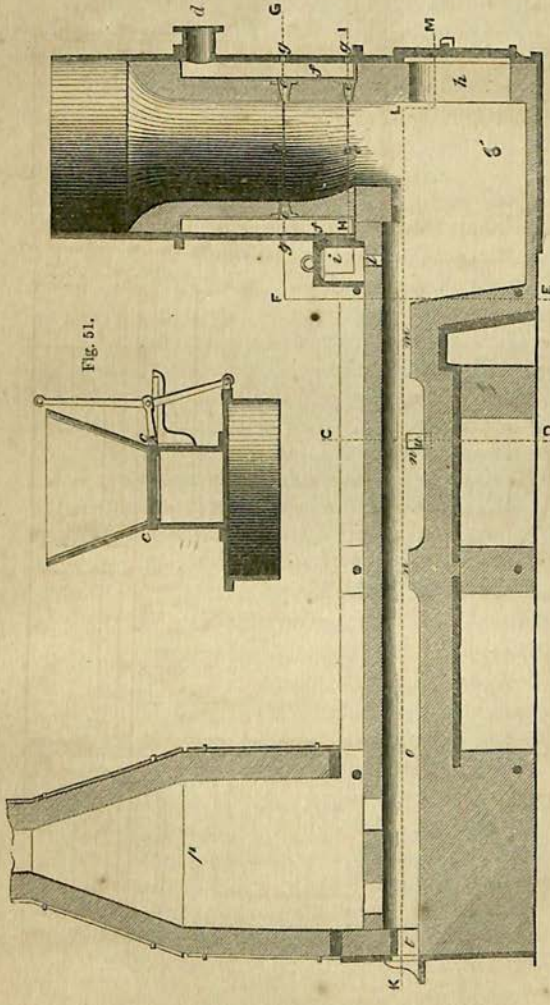


Fig. 51.



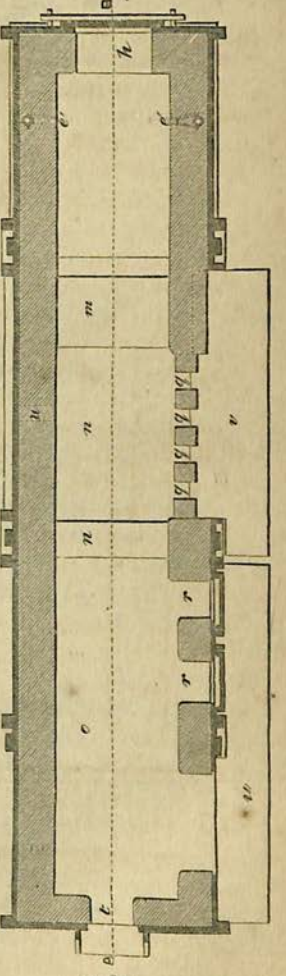


Fig. 52.

furnaces in the same vertical section, it has been necessary to deviate from the actual position of these furnaces at the Mint, where the melting furnace is *not behind*, but on *one side* of, the gas furnace. The atmospheric air is forced by a small fan through the pipes, *f*, *n*, which are provided with regulating valves.

The other furnace to be described is in use at Ekman's Iron-works in Sweden for re-heating slabs and bars of iron. In 1848 Mr. C. Ekman gave me drawings of furnaces of this kind, which, he informed me, had been in successful operation during several years previously. The accompanying woodcuts have been executed from engravings in the Jern-Kontorets Annaler for 1850, which, with the exception of some differences in minor details since introduced, have been copied by Tunner in his account of the Swedish iron manufacture published in 1858.[7] In this place I shall merely describe the arrangement for generating and effecting the combustion of the gas; wood charcoal is the fuel employed. Fig. 49. Side elevation of the furnace.—Fig. 50. Elevation of the gas-generating chamber, which I will call the gas-chamber, on the line EF, fig. 52.—Fig. 51. Vertical section on the line AB, fig. 52.—Fig. 52. Horizontal section on the line KLM, fig. 51.—Fig. 53. Horizontal section of the gas-chamber on the line FG, fig. 51.—Fig. 54. Horizontal section of the gas-chamber on the line HI, fig. 51.—Fig. 55. Vertical section on the line CD, fig. 51.

The gas-chamber, *a*, is built of fire-brick, and is enclosed within a jacket of cast-iron, a free space, *f*, *f*, being left between the two. In the wall of this chamber there are two rows of twyers, *e*, *e*, *e*, etc., the upper one containing four and the lower one three. In the iron jacket is a pipe, *d*, through which cold air, at a pressure of about one inch of mercury, is introduced into the space *f*, *f*. The blast in its passage through the space *f*, *f* becomes heated to from 90° to 150° C. (Tunner). In the iron jacket opposite the twyers are small corresponding holes, *g*, *g*, *g*, &c., fitted with movable plugs. On the top of the gas-chamber is a hopper, *b*, having a sliding bottom, *c*, *c*, through which fuel is supplied: near the bottom of the chamber are two twyers, *e'*, *e'*, one on each side. The gas-chamber communicates with the body of the furnace at the fire-bridge, *m*. In the roof of the furnace, on the right of the fire-bridge, is a series of openings, *l*, *l*, &c., connected above with an iron box, *i*, having an easily movable lid, and communicating with the free space, *f*, *f*, by two iron pipes, *k*, *k*, provided with stopcocks. By this arrangement the air entering through the pipe, *d*, passes in part into the interior of the gas-chamber, and in part into the box, *i*, from which it descends through the openings, *l*, *l*. When the gas-chamber is filled with ignited fuel, and air is injected through the pipe, *d*, carbonic oxide is copiously produced, which in its way towards the fire-bridge, *m*, is met by currents of heated air from the openings, *l*, *l*, &c., and is thereby effectually burned. In Tunner's engravings the blast, instead of being thus divided, is a continuous sheet of air; and the lower twyers, *e'*, *e'*, are omitted. Mr. C. Ekman assured me that in a

[7] Das Eisenhüttenwesen in Schweden, Freiberg, 1858.

furnace of this description sufficient heat might be generated to melt *wrought*-iron by the hundredweight. The atmosphere of the body of this furnace may be made either *oxidizing* or *reducing* at will, by suitably regulating the blast passing into the gas-chamber and that descending near the fire-bridge. It is scarcely necessary to observe that if coal is used, it should not be of a *caking* quality. It is probable that anthracite and the slack of free-burning bituminous coal might be advantageously used in these furnaces. Peat artificially dried, but not charred, is extensively used in Sweden in similar furnaces.

I am not aware whether any of these so-called gas-furnaces have been erected in this country. As soon as I received the drawings from Mr. C. Ekman, in 1848, I submitted them to the inspection of several iron-masters in South Staffordshire, but I could not induce any of them to incur the expense of building a furnace for trial. I am desirous of directing the attention of British metallurgists to these furnaces, with a view to the solution of the important practical question of the best means of economizing the small free-burning coal-slack, of which enormous quantities continue to be wasted in the collieries of South Staffordshire and other districts.

Hydrogen.—Hydrogen in admixture with carbonic oxide, generated by passing high-pressure steam through cast-iron retorts filled with coke and heated to bright redness, has been employed in iron-smelting furnaces. This gaseous mixture was first applied, I believe, by my friend Mr. John Dawes, at the Oldbury furnaces, near Birmingham. He obtained a patent for the process, which I saw in operation at these furnaces during several years. It was, however, discontinued; but my friend Mr. William Dawes, a brother of the patentee,[8] informs me that he has lately resumed its use in blast-furnaces in Yorkshire. The composition of this gas has been given at p. 195. It requires a considerable amount of fuel to keep the retorts sufficiently hot to furnish a copious and continuous current. The carbonic acid might be easily separated by means of a lime-purifier, such as is used for purifying gas in gas-works.

Hydro-carbons.—These gases are always generated when wood, lignite, or bituminous coal is employed as fuel; and the flame in reverberatory furnaces is chiefly the product of their combustion.

Concluding Observations on Fuel.

Comparison of fuels in regard to calorific power.—I am not aware whether any researches have been recently made to determine the calorific powers of fuels in common use by accurate methods, such as were employed in obtaining the results in the table, p. 58. Rumford and Hassenfratz ascertained the calorific powers of various kinds of wood by means of the ice calorimeter, in which the number of the units of heat evolved by the combustion of a substance is deduced from the amount of ice melted.[9]

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[8] Mr. John Dawes has long withdrawn from the iron trade.

[9] Traité de la Chaleur. Peclet. 2nd ed. Paris, 1843. 2, p. 60.

The results of these observers were as follow :—

	Units of heat from 1 part of perfectly dry wood.
Rumford	3654
Hassenfratz	3675

Calorific power calculated from ultimate composition.—The mean ultimate composition of dry wood, inclusive of nitrogen and ash, as deduced from the table of Chevandier's analysis :

		In round numbers.
Carbon	50·32	50
Hydrogen	6·13	6
Oxygen	40·73	41
Nitrogen } Ash }	2·82	3
	100·00	100·00

The number of units of heat evolved from the perfect combustion of 1 part by weight of *dry* wood will be as follow :—

		Units of heat.
Carbon	0·50 will yield $\frac{8080}{2}$	= 4040
Hydrogen, in excess,	0·01 ditto $\frac{34000}{100}$	= 340
Total		4380
Deduct latent heat of water supposed to pre-exist in the wood and that derived from the hydrogen in excess	0·55 × 537 =	295
		4085

If the water supposed to pre-exist be regarded as in the solid state, it will be necessary to deduct the latent heat of fusion of this quantity of water, namely, 0·46 × 79·2 = 36·43 ; 4085 − 36·43 = 4048·22.

In calculating the calorific power of air-dried wood, it will be necessary to deduct the latent heat of the hygroscopic water. Estimating this water at the average amount of 20 per cent., the calorific power will be deduced as follows :—

Composition of 1 part of air-dried wood, containing 20 per cent. of hygroscopic water :—

Carbon	0·400
Hydrogen	0·048
Oxygen	0·328
Hygroscopic water	0·200
Nitrogen and ash	0·024
	1·000

		Units of heat.
Carbon	0·400 will yield	3232
Hydrogen, in excess,	0·070 ditto	238
Total		3470
Deduct latent heat of total water from every source, exclusive of latent heat of fusion of the water supposed to pre-exist	0·632 × 537 =	339
Calorific power of ordinary air-dried wood		3131

The foregoing results lead to the conclusion, previously announced, that the amount of heat developed by the perfect combustion of wood is equal to that which would be produced by the perfect combustion of the carbon and of the hydrogen in excess of that required to form water with the oxygen present, supposing these elements were isolated. The rest of the hydrogen therefore may be regarded, so far as relates to calorific power, as in combination with oxygen in the state of water. But air-dried wood contains a large quantity of hygroscopic water, which, together with the water represented by the oxygen and hydrogen assumed to exist in combination in the tissue of wood, must, during combustion, be converted into steam with the consumption of a large amount of heat. Hence, in certain metallurgical processes requiring a high temperature, in which wood is employed as fuel, it has been found desirable to subject it to a preliminary desiccation at a temperature almost sufficient to occasion incipient charring.

Calorific power of other kinds of fuel.—The conclusion above stated respecting the calorific power of wood is believed to apply equally to all other kinds of fuel containing oxygen; so that the theoretic calorific power of any fuel may be immediately deduced from its ultimate composition. The calorific powers of various kinds of wood, peat, and coal have been calculated in this manner as well as by Berthier's process; and their evaporative powers have also been determined by experiments with steam-boilers on a large scale. Such information, however, has not that practical value for the metallurgist which might at first be supposed. The manner in which fuel burns is of great importance, and this may depend essentially upon its physical properties. Thus, particular qualities of charcoal, coke, and anthracite may have the same calorific power and yet differ remarkably in their manner of burning. Of the three, charcoal, being very light and porous, ignites most easily, and in a given volume contains the least combustible matter; and, accordingly, under the same conditions it is most quickly consumed. Coke also contains less combustible matter in a given volume, and, except when prepared at high temperatures, is more easily ignited, than anthracite. The practical effect of these differences in the manner of burning will be well understood by experimenting on these three kinds of fuel in a common casting furnace about 1 foot square and from 2 to 3 feet deep. If an attempt is made to heat a large crucible in such a furnace by means of anthracite, it will be found that the bottom becomes heated to whiteness before the top is hardly red-hot; whereas by the use of coke the temperature is not so excessive at the bottom, but is much more equally diffused through the furnace. The effect of anthracite as a fuel is the rapid production of an intense heat confined to a space not extending beyond a few inches above the bars.[1]

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[1] It is obvious that on this account anthracite is not adapted as a fuel for ordinary steam-boiler furnaces; but by the following simple contrivance it may be advantageously employed in these furnaces. The ash-pit is kept filled with

In illustration of this property of anthracite I may mention the following experiment:—At the School of Mines there is a small air-furnace, 8 inches square, and 20 inches deep, connected with a stack about 60 feet high. In this furnace, which was quite cold at the beginning of the experiment, but the stack of which was strongly heated by adjoining furnaces, a considerable quantity of manganese was reduced and well melted by means of anthracite within 40 minutes from the lighting of the fire.

Some bituminous coals may be nearly, if not absolutely, identical in ultimate chemical composition, and may, consequently, have the same calorific power; yet, with respect to their manner of burning, they may be widely dissimilar. In the selection, therefore, of coal, the metallurgist must not be guided merely by the consideration of its calorific power, but must in every case trust only to the results of actual trials in furnaces on the large scale. He should not, as I have seen some *practical* men do, attempt to judge of coal from its external appearance. One variety of coal may be approved of simply because it is "bright," and another condemned simply because it is "black;" and yet the latter may for certain metallurgical operations be equal, if not superior, to the former. Both kinds may occur in the same pit, when the "bright" will generally fetch a much higher price than the "black," for no other reason, in some cases—I do not say all—than the mere prepossession of the purchaser in favour of the "bright."

Evaporative power of coals.—In regard to the evaporative power of coals, a few remarks may not be altogether out of place in this work. Numerous costly and very elaborate experiments have been made in this and other countries to determine the relative values of different kinds of coal with reference to steam navigation; and I have no hesitation in expressing my conviction that the results may lead to very erroneous conclusions. A particular boiler—it may be an old one—is selected for the purpose of experiment, and set over a particular fire-grate, &c. We will suppose two varieties of coal, say A and B, to be tested in this apparatus, and that, weight for weight, A is found to yield more steam than B; whereupon A is pronounced decidedly superior as a steam coal to B. But it is quite possible to con-

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water, and deep fish-bellied bars are used, of which the lowest parts nearly, if they do not actually, touch the water. Steam is necessarily evolved from the surface of the water, and enters the fire-place along with the atmospheric air which sustains combustion. On passing through the incandescent anthracite, it is decomposed, with the formation of the combustible gases, carbonic oxide and hydrogen, which are afterwards burned under the boiler at a distance from the fire by the admission of a suitable supply of atmospheric air from without. The decomposition of the steam causes a considerable diminution of temperature within the fire-place; but there is no permanent loss of heat, as, on the subsequent burning of the combustible gases derived from the steam, the heat absorbed in the first instance is again given out and economized: there is, so to speak, only a transference of heat from the fire-place to a distance. The bars do not become sufficiently heated to burn rapidly away. The fire-place should be enclosed above by a fire-brick arch, as no part of the boiler should be unprotected above the solid fuel. The arrangement which I have described I saw in practice some years ago at Messrs. Watney and Son's distillery at Wandsworth, and it appeared to be quite successful.

ceive that under another boiler, and with another form of fire-grate, &c., B might be found far superior to A. Experiments, indeed, have in some cases established that such is actually the case.

Stacks or chimneys.—I have not entered specially in this place upon a consideration of the passage of air through stacks or chimneys. The subject is one of great intricacy; and I doubt whether the laws which have been established concerning the passage of gases through tubes of various kinds will admit of being in many cases applied with success to the construction of stacks in metallurgical works. The nature and varying condition of the internal surface of the stacks, their different forms, the inclination of flues connecting the furnaces and stacks together, the existence of angles, &c., all combine to render difficult the application of exact formulæ obtained on the small scale under simple conditions.

NATURAL REFRACTORY MATERIALS,

EMPLOYED IN THE CONSTRUCTION OF

CRUCIBLES, RETORTS, FURNACES, &c.

FIRE-CLAYS.

CLAYS are termed *fire-clays*, or *refractory clays*, when they resist exposure to a high temperature without melting or becoming in a sensible degree soft and pasty. These clays differ much in the degree of their refractory quality. They occur in various geological formations, old as well as recent; but some of the best abound in the coal measures.

All clays as they occur in nature are essentially *hydrated* silicates of alumina; and upon the presence of the water of *combination* depends their fictile or plastic property, that is, their capability of being moulded into vessels when mixed with water and kneaded to a pasty consistency. All clays contain *hygroscopic* water, which may be expelled at 100° C. without lessening their plasticity. When, however, clay is heated to redness, it loses not only its hygroscopic water, but also its water of combination, and, as a consequence, it ceases to be plastic. In this dehydrated state it cannot again directly *combine* with water and regain its plasticity. It may, indeed, *absorb* water with avidity; but not the smallest degree of plasticity is thereby restored. Pounded brick, for example, is dehydrated clay; and it may absorb a considerable quantity of water without regaining the slightest amount of plasticity.

It is important to note that there may be great variation in the composition and quality of clays which occur in contiguous beds in the same pit, and even of clay from the *same* continuous horizontal bed in the same locality.[1]

If we compare different clays together in respect to elementary composition, we find the relation between the silica and alumina to be extremely variable; and, accordingly, the formulæ which have been proposed to express their rational constitution are very discordant. This is in great measure to be explained by the fact that in many clays a large proportion of silica exists uncombined either as sand, or in a much finer state of division. The grittiness of a clay is due to the presence of sand. Fresenius has investigated the clays of the Duchy of Nassau which are employed in the manufacture of pottery, and has attempted to determine the proportion of free silica which they contain.[2] The sand and much of the finer silica may be separated by the following process of washing, which he adopted. He made use

[1] Brongniart, Tr. des Arts Céramiques, 2, p. 309. Journ. für prakt. Chemie, 57, p. 67.

[2] Journ. für praktische Chemie, Erdmann, 57, p. 64. 1852.

of the efficient apparatus of Schulze for the *mechanical* analysis of soils. It consists essentially of a glass vessel resembling in shape a large champagne-glass, 10 inches high and $2\frac{1}{2}$ in diameter, on the mouth of which is fitted a brass ring, *a*, provided with an elbow-tube, for the outflow of water. A funnel-mouthed tube, *b*, 18 inches long, and about $\frac{1}{4}$ of an inch in diameter, but contracted at the lower end to about $\frac{1}{16}$ of an inch in diameter, is placed in the glass. An ounce of air-dried clay may be operated on at a time. It is prepared by breaking it up and digesting it with a moderate quantity of water in a porcelain basin for half an hour, stirring gently with a pestle all the while. By this means it is thoroughly disintegrated. The mixture of clay and water is then poured into the glass above described. Water from a stop-cock attached to a reservoir is allowed to run into the funnel-mouthed tube, the lower end of which rests on the bottom of the glass. If this precaution were not taken, the tube would become stopped up with clay. The clay is strongly agitated by this continuous stream of water, but only the finer particles are carried upwards and flow out by the side-tube. The water in the supply-tube should be kept at 8 inches above that in the glass. The sand is left at the bottom of the glass, and may be weighed after ignition. The matter removed by the current of water must be allowed to subside, and washed a second time with a column of water about $1\frac{1}{4}$ inch high in the supply-tube. The residue of very fine sand remaining in the glass is collected on a filter, ignited, and weighed. The second washing requires about 10 litres of water, and lasts from 3 to 4 hours. After the determination of the amount of water in the raw clay, the amount of clayey matter carried away in the process of washing may be found by deducting the sum of this water and the residual silica from the total quantity of clay employed in the experiment. Five kinds of air-dried clay yielded by this treatment the following results:—

Fig. 56.
Copied from Schulze's figure.

	1.	2.	3.	4.	5.
Sand	24·68	11·30	8·91	7·74	6·66
Very fine sand or sand-dust	11·29	12·54	10·53	12·19	9·66
Clay	57·34	70·73	71·66	71·70	78·42
Water	6·21	5·43	8·90	8·37	8·86

1. From Hillscheid. 2. From Bendorf. 3. From Baumbach. 4. From Grenzhausen. 5. From Ebernhahn.

These clays were analysed, and the results are worthy of attention.

1. Boiling water extracts a small quantity of organic matter, chloride of sodium and sulphate of lime. The presence of these salts is to be expected, as they are always found in natural waters, and as clay has been deposited by the agency of water.

2. The solution obtained by digesting the clay at a gentle heat with dilute hydrochloric acid contains sesquioxide and protoxide of iron, traces of protoxide of manganese, lime, magnesia, alumina, soda in minute proportion, sulphuric acid, and phosphoric acid as detected by the application of the molybdate of ammonia test. The *insoluble* residue contains silica, alumina, sesquioxide of iron, lime, magnesia, potash, and traces of soda.

3. A boiling solution of carbonate of soda extracts a small quantity of silica, which before ignition in the usual way is yellowish-brown, from the presence of organic matter.

4. When the clay is heated for a considerable time with slightly diluted sulphuric acid, and the temperature towards the last increased so as to expel the excess of the acid, the clayey part is completely decomposed with the separation of nearly the whole of the silica, which may be separated from the sand in admixture with it by boiling with a solution of carbonate of soda.

5. The clay yields decided evidence of the presence of ammonia, red litmus paper being rendered blue when suspended over the clay moistened with a solution of carbonate of soda and warmed.

The composition of the Passau clays was found to be as follows, after drying at 100° C. :—

	1.	2.	3.	4.	5.
Silica	77·03	75·44	62·78	68·28	64·80
Alumina	14·05	17·09	25·48	20·00	24·47
Sesquioxide of iron	1·35	1·13	1·25	1·78	1·72
Lime	0·35	0·48	0·36	0·61	1·08
Magnesia	0·47	0·31	0·47	0·52	0·87
Potash	1·26	0·52	2·51	2·35	0·29
Water	5·17	4·71	6·65	6·39	6·72
	99·69	99·68	99·50	99·93	99·95

In No. 1 the amount of soda was determined, and found to be 0·33 per cent.

By treatment with sulphuric acid the percentage of insoluble residue in the clays dried at 100° C. was as follows :—

	1.	2.	3.	4.	5.
Sand	56·95	47·40	16·20	29·63	18·29
Silica separated from combination	21·13	29·51	46·76	39·50	46·11
	78·08	76·91	62·96	69·13	64·40

On comparing the amount of residue insoluble in sulphuric acid with the total amount of silica given in the tables of analyses of these clays respectively, it will appear that the sand must be nearly pure silica.

By boiling with a solution of carbonate of soda, the percentage of silica dissolved was as follows:—

	1.	2.	3.	4.	5.
Silica	1·39	1·06	1·05	0·91	0·98

In the next table is presented the percentage of silica existing in the different states in the clays dried at 100° C.

	1.	2.	3.	4.	5.
Silica in the form of sand	24·91	11·39	9·13	7·91	6·81
do. do. fine sand[3]	11·40	12·64	7·07[4]	12·45	9·89
do. do. in the finest state of division, and carried over with the clay[5]	20·64	23·37	0·00	9·27	1·59
Total silica existing as sand	56·95	47·40	16·20	29·63	18·29
Silica in the state of hydrate	1·39	1·06	1·05	0·91	0·98
do. combined with bases	18·69	26·98	45·53	37·74	45·53
Total silica	77·03	75·44	62·78	68·28	64·80

In the next table is given the percentage composition of the clays after the deduction of the silica existing as sand, and in the state in which it dissolves in a hot solution of carbonate of soda.

	1.	2.	3.	4.	5.
Silica	45·30	52·74	55·40	54·43	56·48
Alumina	34·08	33·41	31·04	28·85	30·36
Sesquioxide of iron	3·27	2·20	1·51	2·57	2·14
Lime	0·87	0·94	0·43	0·87	1·34
Magnesia	1·14	0·61	0·57	0·75	1·08
Potash	3·05	1·01	3·05	3·39	0·36
Water	12·29	9·08	8·00	9·13	8·24
	100·00	100·00	100·00	100·00	100·00
With 100 parts of clay are associated: Sand	137·03	92·09	19·60	42·70	22·68
With 100 parts of clay are associated: Silica as hydrate	3·59	2·19	1·36	1·40	1·30
The amount containing 100 parts of clay free from sand	240·62	194·28	120·96	144·10	123·98

The addition is wrong in Nos. 2 and 4.

[3] These numbers are somewhat higher than those previously given, because they are deduced from the clays dried at 100° C., whereas the latter were deduced from the *air-dried* clays.

[4] These numbers are found by subtracting the sum of the silica given under the other heads from the total amount of silica in the table of analyses.

[5] This is found by subtracting the sand from the total amount of silica; it is less than that found by the process of washing, which proves that the latter was not free from clay.

As the hydrated silicate of alumina, of which clay essentially consists, cannot be freed from other silicates, with which it is naturally associated, and as the constitution of these silicates is unknown, a rational formula cannot yet with certainty be assigned to clay. If we select the last three clays as containing the least sand, and calculate the ratio between the oxygen of the silica, alumina, and water, we obtain the following results (Fresenius):—

	Silica.	Alumina.	Water.
3.	6	3·02	1·48
4.	6	2·86	1·72
5.	6	2·90	1·49

These numbers would lead to the formula $Al^2O^3,2SiO^3 + 2HO$, if the oxygen of the water be estimated at two-thirds of that of the alumina; or to the formula $2\ (Al^2O^3, 2SiO^3) + 3HO$, if it be estimated only at half that of the alumina. The composition calculated from the first of these formulæ is—

Silica	57·14
Alumina	31·72
Water	11·14
	100·00

This formula is different from those which have been proposed for Kaolin. Thus the formula of Brongniart and Malaguti for this mineral is $3Al^2O^3, 4SiO^3 + 6HO$, while that of Forchhammer is $2Al^2O^3, 3SiO^3 + 6HO$.

In the accompanying tables of analyses of fire-clays I have introduced some bad clays in order that in respect to composition they may be compared with good clays; so that a clear indication may be afforded of the injurious ingredients of a clay. I regret that I am obliged to avail myself of many analyses which are very incomplete, and in so far unsatisfactory; yet they are interesting as showing the relation between the silica and alumina.

Composition of Foreign Fire-Clays.

No.	Locality.	Silica.	Alumina.	Alkalies.	Lime.	Magnesia.	Sesquioxide of iron.	Water combined.	Water hygroscopic.	Observations.
1	France	63·57	27·45	..	0·55	traces.	0·15	8·64	1·27	1. Yellowish. At the highest temperature of the Sèvres porcelain kiln it only frits on the surface. Beleu (Ardennes).
2	Do.	69·42	18·00	..	2·00	3·27	0·95	6·28	2·24	2. Greyish brown. Boulogne (Pas-de-Calais).
3	Do.	44·50	53·00	traces.	1·34	0·60	1·91	16·48	12·87	3. Grey plastic clay, above the chalk. Used for saggars for porcelain. Condé, near Houdan (Seine-et-Oise).
4	Do.	60·60	26·39	..	0·84	..	2·50	9·20	..	4. Infusible at the highest temperature of the Sèvres porcelain kiln. White plastic clay, occurring in the upper fresh-water beds of the Paris basin. Dourdan (Seine-et-Oise).
5	Do.	49·20	34·00	..	..	..	..	16·40	..	5. White plastic clay. Used for crucibles employed in the treatment of ores of antimony. Echassières (Allier).
6	Do.	46·50	38·10	..	traces.	..	..	14·50	0·42	6. Used for saggars for porcelain. Gaujac (Landes).
7	Do.	66·10	19·80	..	..	..	6·30	7·50	..	7. Sandy yellowish clay. Used for fire-bricks. Hayanges (Moselle).
8	Do.	55·40	26·40	..	..	..	4·20	12·00	..	8. Dirty yellowish-white clay. Used for glass pots. Labouchade, near Montluçon (Allier).
9	Do.	52·55	26·50	..	3·00	1·50	0·55	15·00	1·55	9. Veined plastic clay. Used for porcelain saggars at Limoges. Malaise, near Limoges (Hte. Vienne).
10	Do.	52·10	36·00	..	5·00	2·00	1·80	..	..	10. Whitish plastic clay. Used for fire-bricks and porcelain saggars at Sèvres. Provins (Seine-et-Oise).
11	Do.	42·00	38·96	..	1·04	0·17	0·85	16·96	2·27	11. Reddish. Used for porcelain saggars at Sèvres. Retourneloup (Seine-et-Marne).
12	Do.	58·76	25·10	traces.	traces.	2·51	2·50	11·05	1·45	12. Reddish, with scales of mica. Used for crucibles in which cast steel is melted at St. Etienne. Savanas (Ardèche).
13	Hesse.....	47·50	34·37	traces.	0·50	1·00	1·24	14·00	0·43	13. Greyish. Used for Hessian crucibles. Gross-Almerode, Hessen-Cassel.
14	Bavaria.....	45·79	28·10	..	2·00	..	6·55	16·50	0·05	14. Deep grey. Used for Passau crucibles. Schildorf, near Passau.
15	Saxony	61·52	20·92	traces.	0·02	4·97	0·50	11·70	2·70	15. Blackish, contains quartz. Used for porcelain saggars in the Meissen porcelain manufactory. Loshayn, near Meissen.
16	Bohemia.....	58·39	27·94	..	2·74	1·00	traces.	10·00	0·49	16. White, very soft to the touch. Below the lignite. Used for saggars at Elbogen. Thenberg, near Carlsbad.
17	Austria.....	65·60	20·75	traces.	1·65	traces.	2·00	10·00	1·00	17. Pale dirty green, mixed with ferruginous spots. Used for porcelain saggars at Vienna. Gottweith, near Krems.
18	United States	72·33	16·75	..	2·00	0·07	1·29	6·84	1·14	18. Greenish grey, mixed with red spots. Used for porcelain saggars and glass pots. Delaware, 7 miles south of Newcastle.

1, 2, 3, 4, 6, 9, 11, 12, 13, 14, 15, 16, 17, 18. By Salvétat, Traité des Arts Céramiques. Brongniart, Atlas, 1844. See Table No. 5.—5, 7, 8. By Berthier, op. cit.—10. By Buisson, op. cit.

Composition of British Fire-clays.

No.	Locality.	Specific Gravity.	SiO^3.	Al^2O^3.	KO.	NaO.	CaO.	MgO.	FeO.	Fe^2O^3.	MnO.	PO^5.	Water combined.	Water Hygroscopic.	Organic matter.	Observations.
1	Stourbridge, Worcestershire	..	65·10	22·22	0·18	..	0·14	0·18	1·92	..	..	0·06	7·10	2·18	0·58	1. Best clay, used by Messrs. Chance for glass pots. Brown like a clay iron ore in colour. The silica is partly free, gritty sand being separated by washing. No sulphur was detected by boiling with nitric acid.
2	Do. do.	..	63·30	23·30	..	..	0·73	..	1·80	..	..	..		10·30		2. Best Stourbridge clay, such as is used at Messrs. Chance's works.
3	Corngreaves do.	..	57·31	26·58	0·44	..	0·71	0·49	2·83	..	..	trace.	8·52	2·26	0·44	3. Darker than No. 1. Silica partly free. No. 1 and this clay were fashioned into small prisms with sharp edges, and exposed in the same covered crucible to a very high temperature. No. 1 becomes pale brown by burning, and No. 3 grey. No. 1 is decidedly more refractory than No. 3, which is more glazed on the surface. The two trial pieces adhered firmly together where they had been in contact. The alkali was determined with great care. The results were as follow:—
4	Brierley Hill, Staffordshire	..	51·80	30·40	..	trace.	..	0·50	4·14	..	..	..		13·11		By fusion with nitrate of baryta: No. 1 gave 0·20 per cent.; No. 3 ,, 0·43 ,,
5	Do. do.	..	51·70	28·50	..	..	..	0·85	5·85	..	..	..		12·50		By hydrofluoric acid: No. 1 gave 0·16, mean 0·18; No. 3 ,, 0·45 ,, 0·44.
6	Do. do.	..	45·27	28·77	..	..	0·47	..	7·72	..	..	..		17·34		8·09 grains of this clay were boiled with sulphuric acid in a platinum vessel. The insoluble residue weighed 4·955 grains, or 61·24 per cent. The total amount of silica found by fusion with alkaline carbonate was 57·31, so that the decomposition of the clay by sulphuric acid was not complete. The 4·955 of residue was boiled with a solution of carbonate of soda and a little caustic potash during two days: the insoluble residue weighed 2·38, or 29·41 per cent., which in great measure was silica present as sand in the clay.
7	Glascote, near Tamworth	..	50·20	32·59	2·32	..	0·36	0·44	..	3·52	trace.	..	9·69	3·00	..	4. This clay was tried by Mr. Ruel, of Holborn, the well-known crucible-maker, and pronounced by him to be of first-rate quality.
8	Do. do.	..	49·40	32·80	2·24	..	not deter.	0·42	..	3·87	trace.	..	9·84			7, 8. This clay occurs in the coal-measures, and is made into fire-bricks by Messrs. Gibbs, Canning, & Co. We have used this clay during many years at the School of Mines to make small crucibles for the assaying of iron ores by the Swedish method. The iron existed in the two states of oxidation. My friend Mr. Léon
9	Stannington, near Sheffield	..	48·04	34·47	1·94	..	0·66	0·45	..	3·05	..	..	11·15			
10	Ensor, near Derby	..	48·08	36·89	1·88	..	0·55	trace.	..	2·26	..	..	10·87			
11	Newcastle-on-Tyne	2·519	55·50	27·75	2·19	0·44 with Cl and SO^3	0·67	0·75	..	2·01	..	..	10·53 with trace of organic matter	..	..	
12	Teignmouth, Devonshire	..	52·06	29·38	2·29	..	0·43	0·02	2·37	..	..	..	10·27	2·56	..	

13	Poole, Dorsetshire..	..	48·99	32·11	3·31	..	0·43	0·22	2 34	..	..	..	9·63	2·33	..		Arnoux, of Messrs. Minton and Co.'s China-works, informs me that it is extremely good for saggars.
14	Dowlais	..	67·12	21·18	2·02	..	0·32	0·84	..	1·85	..	..	4·82	1·39	with a little CO^2 0·90		9, 10. I received specimens of these clays from Mr. E. T. Sanderson, of Sheffield, by whom they are used for cast-steel pots. They were weighed for analysis after desiccation at 100° C.
15	Do. do. ...	..	44·25	34·76	1·58	..	0·34	1·18	..	3 41	..	traces.	8·56	2·89	3·17		
16	Do. do. ...	..	53·05	28 13	4 19	..	0·17	1·20	..	2·48	..	..	5·82	2·20	2·82	traces of sulphuric acid.	11. Colour grey, streak dull, very soapy to the touch. It constitutes usually the basement of each coal-seam. From Blaydon Burn Colliery in Tyneside. It is used for the manufacture of fire-bricks.
17	Do. do. ...	..	47·29	33·67	2·13	..	0·45	1·06	..	2·52	..	..	9 07	2·19	2·53		
18	Do. do. ...	..	46·26	32·14	2·11	..	0·73	1 21	..	2·99	..	..	8·79	2·77	3·46		12. Light brownish grey, with small dark particles (lignite?) diffused through it. Used in admixture for Cornish crucibles. This must be the Bovey clay, in which lignite occurs, and is called Teignmouth from being shipped at that port.
19	Do. do. ...	..	58·10	26·59	1·21	..	0·40	0·99	..	2·97	..	..	7·57	1·41	1·21		13. Greyish white, soapy to the touch. Used in admixture for Cornish crucibles.
20	Do. do. ...	..	53·99	28·66	1·76	..	0·31	0·88	..	3·27	..	..	7·41	1·52	2·46		14-21. All from Dowlais. No. 14 is considered the best fire-clay at Dowlais. Name of seam Blaen Rhas, three coals and clay. No. 15. Not generally considered good as a fire-clay. From the level Tomos. No. 16. This clay melted down on the bridge of a *balling-furnace*. Red coal. 17. Blaen Rhas, Little Vein. 18. Coal clod. 19. Pantywain. 20. Lower 4 feet 2. 21. Little Pins.
21	Do. do. ...	..	57·10	26·77	1·85	..	0·28	1·07	..	3·10	..	..	6·44	1·76	1·89		
22	Glasgow	..	66·16	22·54	..	..	1·42	trace.	5·31	..	..	..	3·14	..	..		
23	Do. do. ...	2·558	66·68	26·08	..	..	0·84	trace.	1·26	..	..	..	5·14	..	..	dried at 100° C.	22. Coarse, producing a porous body. Well adapted for saggars, glass-pots, crucibles, and fire-bricks.
24	Do. do. ...	..	53·66	32·00	..	..	0·41	trace.	1·35	..	..	..	12·08	..	..	do.	23. Sandy clay. Contains a considerable quantity of sand, and is well adapted for salt-glazed ware.
25	Do. do. ...	..	46·38	38·04	..	..	1·20	trace.	1·04	..	..	..	13·57	..	..	do.	24. Pipe-clay.
26	Ireland.....	..	79·40	12·25	..	..	0·50	..	..	1·30	..	..	5 20	..	..		25. Colour greyish, burns perfectly white, and approaches nearest to China clay.
27	Do. do. ...	..	74·44	19 04	2·07	..	0·45	0·27	..	0·61	..	..	3·71	..	..		26. Small crucibles made of this clay were kept for hours with melted steel in them without in the least changing form.
28	Cornwall.....	..	46·32	39·74	..	..	0·36	0·44	0·27	..	..	..	12·67	12·08	..	"some alkali" is included in the water.	27. I believe this clay was from Howth, near Dublin, and that I received it from Mr. Robert Mallet, who has published the analysis of at least a similar clay, if it be not the same, in the Philos. Magazine.
29	Do. do. ...	..	46 29	40·09	..	..	0·50	..	0·27	..	..	..	12·67	..	..	dried at 100° C.	28, 29. Said to be the finest China clay, Kaolinite, from Cornwall. The two analyses are of the same clay by different men.

1. By C. Tookey.—2. By Mr. E. Cowper.—3. By C. Tookey.—4, 5. By T. H. Henry, communicated to the Author.—6. By Salvetat.—7. By J. Spiller.—8, 9, 10. By Burbidge Hambly.—11. By Hugh Taylor, Edinb. New Phil. Journ., 50, 142.—12, 13. By W. Weston. Nos. 1, 3, 7, 8, 9, 10, 12, and 13, were analysed in my laboratory at the School of Mines.—14-21. By Edward Riley, formerly chemist at Dowlais, communicated to the Author.—22. By John Brown, Phil. Mag. 1847, 31, p. 437.—23. By R. A. Couper, Phil. Mag. 31, 436.—24. By J. Brown, op. cit.—25. By J. Higginbotham, Phil. Mag. op. cit.—26. By T. H. Henry, communicated to the Author.—27. By J. Spiller, in my laboratory.—28. By R. A. Couper, and 29, by J. Brown, op. cit.

CRUCIBLES.

The term crucible is generally applied to earthenware vessels in which metals or other substances are heated in furnaces; but the term is not restricted to vessels of earthenware: it is extended to all open-mouthed movable vessels, of whatsoever material composed, in which substances are in *any* way exposed to high temperatures. Thus, there are crucibles consisting of graphite, iron, platinum, and lime. In English it is usual to confine the use of the term crucible to vessels which can be conveniently handled by means of tongs or forceps, and which are not intended to remain as fixtures in a furnace during any length of time. In French the term crucible (creuset) is applied not only to large movable vessels, but even to the hearth of a blast-furnace. It has been asserted that the origin of the word crucible is due to the superstitious practice of the alchemists of marking these vessels with the sign of the cross; and, as Latin was the language in which they wrote, the word was derived from crux, crucis.[6] Hence the expression *crucial experiment*. The use of superstitious signs is not yet extinct with physicians, for in their prescriptions the prolonged tail of the letter ℞, which is intended as an abbreviation for *Recipe*, is a relic of the astrological symbol of Jupiter.[7]

The qualities which may be required in crucibles, according to the special purposes to which it is proposed to apply them, may be thus enumerated:—

a. They should resist a high temperature without fusing or softening in a sensible degree.

b. They should not be tender while hot, so as to be liable to crumble or break when grasped with tongs.

c. In some cases they should resist very sudden and great alternations of temperature, so that they may be plunged while cold into a nearly white-hot furnace without cracking. In other cases it is only necessary that they should resist a high temperature after having been gradually heated.

d. In some cases they should withstand the corrosive action and permeation of such matters as melted oxide of lead.

e. They should all resist sufficiently well the corrosive action of the ashes of the fuel with which they may be surrounded.

I am not aware that any crucibles have been made which combine in the highest degree all the qualities above mentioned. Crucibles must, therefore, be selected with special reference to the conditions to which it is intended to expose them.

Earthen or clay Crucibles.—These crucibles are made of fire-clay in admixture with silica, burnt clay, or other infusible matter. When clay is dehydrated by heat, it contracts considerably; and even after

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[6] Johnson's Dictionary, London, 1805, 9th ed. Longman and Co. "Crucible—a chymist's melting-pot, made of earth: so called because they were formerly marked with a cross."

[7] Pharmacologia. By J. A. Paris, M.D., F.R.S., 8th ed., 1833, p. 13.

the complete expulsion of its water of combination it may suffer much further contraction by exposure to a higher degree of heat. Wedgwood in the construction of his pyrometer availed himself of the property which clays thus possess of shrinking or contracting in a degree corresponding to the degree of heat to which they are subjected. In proportion to the amount of contraction which a clay crucible suffers when heated will be its liability to crack. In order to counteract as far as practicable the evil due to contraction, clay crucibles are made of a mixture of clay and of some other substance, which either expands somewhat by heat, or at least does not contract in a sensible degree. The other qualities required in the substance added are infusibility at high temperatures, and freedom from any tendency to fuse or soften the clay, conditions well fulfilled by highly burnt fire-clay, silica, and carbon in the state of graphite or coke.

The unburnt clay must be reduced to powder by grinding; and complete disintegration may be effected by allowing the clay to be freely exposed to the action of the weather during a considerable time, especially the winter season. The burnt clay is generally prepared by grinding crucibles which have been used, or, still better, glass-pots which have been exposed to a high temperature during a long time. Failing these materials, fire-clay may be burnt expressly for the purpose. Before grinding up pieces of old pots, their surfaces, which are generally more or less vitrified, and have extraneous matter adhering to them, should be carefully chipped off. The size of the particles of burnt pot is a matter of importance. Brongniart insists that variation in the size of the particles is an advantage. The proportion of burnt to raw clay may be altered according to circumstances. A mixture of about $\frac{3}{4}$ by measure of raw clay to $\frac{1}{4}$ of burnt clay is suitable for many crucibles. But on purely practical points of this kind experience alone will enable the operator to decide.

The addition of an infusible substance like silica, graphite, or coke to raw clay may not only tend to counteract the evil due to contraction of the clay, but may also fulfil another important purpose. Crucibles composed of good fire-clay may be softened and lose their shape at the high temperatures occasionally produced in furnaces. In such a case the presence of an infusible substance may act, as it were, the part of a rigid skeleton to the crucible, and prevent its collapsing in the furnace. According to Berthier, if silica be employed, it may, by long exposure to a high temperature, gradually enter into combination with the clay, and form a more or less homogeneous and pasty mass: and this evil will be specially likely to occur if the particles of silica are too fine.[8] In all mixtures intended for crucibles, it is requisite that there should be a sufficient quantity of raw clay to produce the proper degree of plasticity for working.

It is important to note that the fusibility of a crucible or fire-brick may not be altogether dependent on its *ultimate* composition, but that it may to a certain extent depend upon the manner in which its *proximate*

[8] Traité des Essais, 1. 66.

constituents are mixed. Granite affords a fitting illustration of this fact. This rock consists, as is well known, of an agglomeration of quartz, felspar, and mica, in particles of considerable size, comparatively speaking. Now, when a piece of granite is exposed even to a very high temperature, it will not melt; but if it is reduced to powder and then similarly heated, it will melt with facility.

The selection of a fire-clay for the manufacture of crucibles should be carefully made, especially in the case of those of large size in which a valuable metal is to be melted. Attention should be particularly directed to the presence of iron pyrites, which in clays from the coal-measures may exist irregularly disseminated in particles. When a crucible made of such clay is heated strongly for any length of time, little cavities, or even perforations, will be produced in the substance of the crucible wherever particles of pyrites may have been imbedded. The pyrites is converted into oxide of iron by oxygen derived from the gases of the furnace, which readily permeate most crucibles. It might be supposed that at the high temperature of our furnaces filled with ignited fuel oxidation could not at any time occur; yet that it may occur I have ascertained experimentally by thus heating crucibles in the substance of which particles of iron pyrites had been expressly imbedded. When the experiment is made by substituting small pieces of chalk for iron pyrites the result is the same. The presence, however, of a small quantity of lime uniformly diffused through a fire-clay may not be injurious, and may possibly tend to render the substance of a crucible made of such clay compact and close in grain. The presence of potass or soda in sensible proportion in a fire-clay would certainly make it less refractory; but in the proportion in which they appear to exist in some of the best fire-clays their effect may be beneficial rather than otherwise, by soldering, as it were, the particles firmly together. I believe that the presence of fixed alkali may be detected in all clays; and no analysis of a clay should be considered of much practical value in which its proportion has not been determined. Potass appears to be present more frequently and in greater quantity than soda; but the late Mr. Henry informed me that in certain Welsh fire-clays he found from 1½ to 3 per cent. of soda. As all clays appear to be the result of the slow decomposition of felspar or some other similar mineral, which contains either potass or soda, by the action of water, the retention of some of the alkali in the residual clay might be expected.

The quality of a fire-clay in reference to its fitness for the manufacture of crucibles may be satisfactorily tested on a small scale, either in an air or small blast-furnace. For this purpose it should be kneaded with water and fashioned into small prismatic pieces with *sharp* edges; and these when dry should be enclosed in a covered crucible and subjected to a very high temperature. The edges of the pieces should afterwards be examined: if they continue sharp, the clay may be regarded as very refractory; but if they are much rounded, it is an evidence at least of incipient fusion; if the pieces are melted down, the clay is worthless. With a little practice in experiments conducted in

this way very satisfactory results may be obtained. It is necessary to enclose the trial pieces in a crucible in order to eliminate the effect of the ashes of the fuel.

The quality of a clay crucible may be readily determined by an actual trial under the special conditions to which it is intended to be subjected. To test the property of resisting corrosion, protoxide of lead, or, still better, a mixture of that oxide and dioxide of copper, may be melted in the crucible. If a clay crucible will stand this test for any length of time without being permeated or corroded in a very sensible degree, no other need be applied. Generally, after such a trial of a few minutes only, ordinary crucibles will be very much corroded and perforated. The substance of the crucible will not be uniformly removed, but will be found to be eaten away irregularly into cavities; and perforation will, probably, only have taken place in one or two spots. The grain of ordinary clay crucibles is very irregular, owing to the nature of the mixtures of which they are made; and hence the great irregularity of action of the oxide of lead. It may now be conceived how regularity of structure and fineness of grain should tend to insure uniformity in the corrosive action of the oxide of lead, and so to prevent perforation.

It is necessary to distinguish between simple infiltration and permeation due to corrosion. The body of some crucibles may be so porous as to admit of their being readily infiltrated by liquids which exert no corrosive effect. As a general rule, clay crucibles will resist permeation and corrosion in proportion to their fineness and regularity of grain; but, unfortunately, in the same proportion is their liability to crack increased. The property of resisting corrosion is not necessarily connected with that of infusibility or softening at very high temperatures; but rather the reverse.

Crucibles are used both in the *unburnt* and *burnt* state. Small crucibles are generally kiln-burnt before they are used. The large Stourbridge clay crucibles or "casting-pots," which are extensively employed in the brass foundries of Birmingham, are never previously burnt. They are gradually and thoroughly dried by the maker in chambers artificially warmed; and are generally kept by the founder in a dry warm situation on shelves in the casting-shop. They will hold forty pounds or more of melted brass. In Birmingham these crucibles are heated in rectangular air-furnaces, about 10 inches square and 2 feet deep. The fuel used is coke. When the furnace is cold, the fire is made and covered to the depth of a few inches with coke, upon which the crucible is placed *inverted*. The furnace is then filled with coke, and the crucible is *gradually* heated to redness. When red-hot it is taken out of the furnace, and immediately put in again with the mouth upwards. When the furnace is hot, and a fresh pot is needed, the fire must be allowed to go down, and the second pot heated with the same precautions as the first. If the pots were put into the furnace at first with the mouth upwards, they would almost certainly crack, notwithstanding every precaution. I have made numerous attempts to use crucibles of the same size and make, after having been kiln burnt, but

I could not succeed in heating them to redness without cracking; although for special reasons I was very desirous of doing so.

It may be stated as a general fact that the tendency of an earthenware crucible to crack increases with its size and thickness. In the case of crucibles which are used in the burnt state, it may also be observed that their liability to crack is increased by *over-firing* during the process of burning them in kilns or otherwise.

Stourbridge clay Crucibles.—The materials used in admixture with the clay are burnt clay and coke. The burnt clay is obtained by pounding and grinding old glass-pots, from the surface of which any adherent glass has been carefully chipped off: only the best Stourbridge clay is used in the making of these pots. The clay is ground under edge-stones, which revolve on edge in the usual way round a circular bed, and the ground clay is passed through a sieve. Thus prepared, it is next mixed with the proper amount of burnt clay and water, and kneaded by men who tread barefoot upon it until it has acquired the right degree of consistency. These crucibles are made by hand in the following way. The workman sits before a bench, in which is a wooden block of the shape of the cavity of the crucible. At the widest end of the block is a flange or projecting border of the same width as the wet crucible is to be made thick at the mouth. In the middle of the same end an iron spindle is inserted, which fits into a socket in the bench. The block may thus be made to revolve in the position indicated in the annexed woodcut; it is not fixed, but may be taken out or dropped into the socket at pleasure. On the narrow or upper end of the block is placed a lump of tempered clay, which the workman then moulds round the block by first striking it with a flat piece of wood, and then slapping with both hands, so as to turn the block more or less each time, as occasion may require. The clay is thus rapidly extended over the whole block down to the flange. A sliding vertical gauge is fixed in the bench near the block, by means of which the thickness of the sides and bottom of the crucible may be regulated. As soon as the moulding is finished, the block is lifted out of its socket and inverted, when the crucible, with a little easing, will gently drop off. The spout for pouring out metal is then fashioned by the finger. The clay may likewise be moulded upon a linen cap wetted and slipped over the block, so that, on inverting the block, the crucible and cap slide off together, after which the cap may be easily pulled out. The wet crucible must be very gradually dried. These crucibles are very extensively employed by brass-founders in Birmingham. After they have been once used in the furnace and allowed to become cold, they are worthless. They are largely manufactured by Messrs. King of Lichfield Street, Birmingham; and I can testify to the excellence of the articles of that firm from an experience of 20 years. The muffles which they have made for me of the same materials as their crucibles are superior in every respect to any others which I have tried. They make 25 sizes of crucibles; the smallest contain 10 lbs. of metal, and

Fig. 57.

sell at 2*s.* per dozen, and the largest 140 lbs., and sell at 11*s.* 3*d.* per dozen in the unburnt state.

A convenient mould for making crucibles is represented in the annexed cut, which is a vertical section through the centre. *a* is a vessel of cast-iron, exactly similar in shape to a common flower-pot, open at the top, and perforated at the bottom; *b* is a disc of wrought-iron, having a spindle fixed in the centre; *c* is a flat ring of cast or wrought iron, of which the internal diameter is less than that of the upper end of *a*,—it is made with a rim on the under side, which loosely clips the top of *a*; *d* is a plug of cast-iron, which passes through and rests on *c*,—it should be turned in a lathe; *e* is empty space round the depending part of the plug, in which the crucible is to be moulded. To this end the mould must be placed on a solid block of wood, in the centre of which is a hole to receive the spindle of *b*; the plug is then withdrawn, and a lump of clay, somewhat more than sufficient for one crucible, is put into the vessel *a*, on the top of the disc or piston, *b*; the plug is then rammed home by means of a suitable hammer until it comes to the position in which it is shown in the woodcut; the superfluous clay escapes through the ring or cover, *c*, around the plug. The space *e* is thus solidly filled with clay, and a crucible formed. The plug is then taken out, the disc, *b*, forced up by means of the spindle, and the crucible raised out of the mould. A spout may then be fashioned by hand in the usual manner, and the crucible removed to a suitable place to dry. In 1762 a patent was granted to William White for a "new invented manufacture of crucibles for the melting metals and salts," &c. The specification directs that Stourbridge clay and Dorsetshire clay are to be mixed with Woolwich sand and water; and that the mixture is to be trodden with the feet.[9] The use of coke in admixture with Stourbridge clay in the manufacture of crucibles was patented by Anstey: he directed that two parts of fine ground raw Stourbridge clay should be mixed with one pint of the hardest gas coke, previously pounded and passed through a sieve of half-inch mesh.[1]

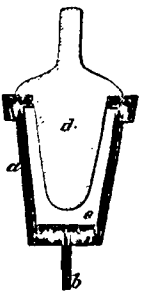

Fig. 58.

Cornish Crucibles.—These crucibles are manufactured on a large scale in Cornwall for the use of copper-assayers. According to Price the first manufactory of these crucibles was established at Truro a few years before the publication of his well-known work;[2] and a premium was awarded to the inventor of them by the Society of Arts. They are generally made round, and of two sizes, of which one fits into the other. Those of the larger size are 3 inches in diameter at the top and 3¼ inches high, outside measure. They are coarse in grain, and their surface has a grayish-white colour. They are spotted both within and without with minute dark coloured specks, due, no doubt,

[9] A.D. 1762. Jan. 25. No. 767.
[1] A Dictionary of Arts, &c., Dr. Ure, 1839, p. 376.
[2] Mineralogia Cornubiensis, 1778, p. 32.

to the presence of minute particles of oxide of iron. Their external surface frequently presents more or less of reddish-brown coloration. They are always kiln-burnt. They may be plunged into a "hot" furnace without cracking; but they become soft at a white heat. This quality of resisting sudden and great alternations of heat will only apply to crucibles not exceeding the dimensions stated above, as we find that those of larger size are very liable to split from top to bottom even when gradually heated. Of all crucibles, however, none are more generally useful for metallurgical experiments. There are two well-known makers of these crucibles, Juleff of Redruth, and Mitchell of Truro. We have made exact comparative trials of the crucibles of both makers, and we believe them to be equally good for the purposes for which they are intended. They are rapidly corroded by melted oxide of lead, but Juleff's much less so than Mitchell's. In shape Mitchell's are more regular than Juleff's; but this is not a material circumstance. The following analysis of one of a batch of Juleff's crucibles, which were found on trial to be excellent, was made by Mr. A. Dick in my laboratory :—

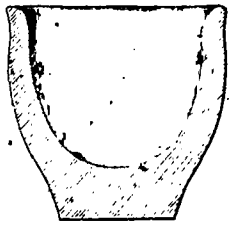

Fig. 59. Section of Cornish crucible, to the scale of ½.

Silica	72·39
Alumina	25·32
Sesquioxide of iron	1·07
Lime	0·38
Magnesia	trace.
Potass	1·14
	100·30

Large crucibles are made of a mixture consisting of

Teignmouth clay	1 part.
Poole clay	1 do.
Sand from St. Agnes's Beacon, Cornwall	2 do.

The composition of these clays will be found in the table, p. 214.

When smaller and less refractory crucibles are needed, the same mixture is employed, with the addition of an eighth-part of China-clay or Kaolinite from St. Austell. I am indebted to Mr. Juleff for this information, which was kindly obtained for me by Mr. John Garby of Redruth, so well known for his knowledge of Cornish minerals. In these crucibles we have an illustration of the use of silica in admixture with clay.

London Crucibles.—These crucibles have a reddish-brown colour, and are close in grain. We find them very liable to crack, so that they require special precautions in their management. In reference to assay-crucibles of this kind manufactured by Ruel, of High Holborn, the late Mr. Henry reported to the Jury of the Great Exhibition in London, 1851, that "they resist the action of fused oxide of lead much better than any he had tried."[3] This accords with the experience obtained

[3] Jury Reports, p. 585.

in our metallurgical laboratory. During recent years we have had good earthen crucibles from the Patent Plumbago Crucible Company, Battersea Works, under the management of Mr. Morgan. They are well moulded and very refractory; they have a smooth surface, and withstand the action of fluxes satisfactorily. They resemble crucibles of the best French make in appearance, but are considerably thicker; I am informed that the firm employs some French workmen, and imports foreign clay. They are known as *white fluxing-pots*. Excepting the very small ones, we find that they are liable to crack when exposed to sudden alternations of heat; and that towards the bottom they are apt to become fissured within, though not sufficiently so to allow the contents to escape. In this respect they are inferior to similar crucibles of French manufacture; a circumstance which may, probably, be due to their too great thickness. After having been once used and allowed to become cold, they are very liable to crack on being reheated. The term *white fluxing-pot* is given to these crucibles in order to distinguish them from the well-known variety of crucibles called *London crucibles*, the name of London serving to indicate *the kind of crucible*, rather than *the place of manufacture*. The smallest are 2¼ inches high, and sell at 1*s*. per dozen; and the largest are 8½ inches high, and sell at 16*s*. per dozen. Annexed is a woodcut of the section of one of medium size, to the scale of ⅓, or 4½ inches high, of which the selling price is 4*s*. per dozen.

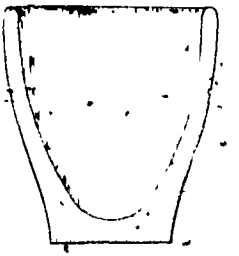

Fig. 60. Section of London crucible, to the scale of ⅓.

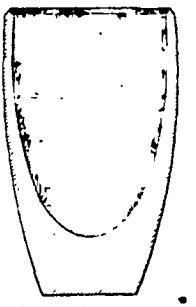

Fig. 61. Section of white fluxing-pot.

Hessian Crucibles.—These crucibles have long had a high reputation, and formerly were those most frequently employed in chemical laboratories. They are generally triangular in shape, so that metal may be conveniently poured out from each corner. They are usually sold in "nests" of six crucibles, which gradually diminish in size so as successively to fit into each other. Crucibles which I have purchased as Hessian in England, and tried during many years, have not justified the high reputation for refractory quality to which, I cannot doubt, the genuine and properly made Hessian crucible is entitled. They are readily permeated by melted oxide of lead. In the character of their body, and in composition and qualities, they closely resemble Cornish crucibles. They are made of a mixture of equal weights of Almerode clay and sand.[4] According to the analysis of Berthier, the Hessian crucible is composed of

Silica	70·9
Alumina	24·8
Sesquioxide of iron	3·8
	99·5

[4] Lehrb. der chemisch. Technologie. Dr. F. Knapp, 1847, 1, p. 598.

Wurzer appears to have analysed at least several Hessian crucibles as he has given the amount of variation in the proportion of each ingredient.[5] He has also analysed the Almerode clay, which he found to consist of

Silica	10·1
Alumina	65·4
Oxide of iron	1·2
Carbonate of lime	0·3
Water	23·0
	100·0

This result is so entirely opposed to that of Berthier, who analysed the same clay, and to all other analyses of fire-clays, that Wurzer's results are, doubtless, erroneous. However, he mentions the presence of titanic acid, which, according to the recent investigation of Riley, may be detected in all fire-clays.[6] The presence of titanic acid to the extent of 1 per cent. in the clay of Gross-Almerode and in a clay from another locality had been previously announced in 1853.[7] But so long ago as 1835 a paper appeared in 'The Philosophical Magazine' on the presence of this acid in Hessian crucibles, by Brett and Bird,[8] who made four analyses, in which the minimum of titanic acid is 3·5 per cent., and the maximum 21·0 per cent. However, their method of analysis cannot be regarded as satisfactory. In consequence of this paper the presence of titanic acid was sought for in the substance of Hessian crucibles by Schwarzenberg in Wöhler's laboratory, but none was detected. Wöhler concluded, therefore, that Messrs. Bird and Brett had mistaken silica or alumina, or both, for titanic acid.[9]

French Crucibles.—Berthier speaks highly of the "creusets de Paris," which are manufactured by Beaufay. He states that, compared with Hessian, they are quite as refractory, equally resist sudden alternations of temperature, and retain melted litharge much longer. They are made of about one part by weight of clay from Andennes and two parts of the same clay burnt and coarsely pounded. They are fine in body. In order that their surface may be very even, they should before using receive a thin coating, both inside and outside, of pure clay. A piece of these crucibles heated to 150° (Wedgwood's pyrometer) became a little rounded upon the angles and edges, but without losing its form, and acquired the smooth, shining fracture of stone ware: its surface became copper-red.[1] Water easily exudes through them. The crucibles termed "creusets de Saveignies," which are manufactured near Beauvais by Deyeux, are thus described by Berthier. They are well moulded, thin, of uniform thickness throughout, and very even; they are fine and homogeneous in grain; they are porous; they retain water, but not sufficiently to prevent the outer surface from being rendered moist; they resist sudden alternations of heat and cold without

[5] Kerl, Handbuch, 1, 136.
[6] Riley on Titanic Acid. Quarterly Journ. of the Chemical Society, 1858.
[7] Kenngott, Uebersicht, etc., 1856, p. 161.
[8] V. 6, p. 113.
[9] Ann. d. Phys. u. Chem. 35, p. 527. 1835.
[1] Traité des Essais, 1, p. 68.

breaking. They are more refractory than those of Beaufay; for when a piece is heated to 150° it retains its granular texture and does not present the fracture of stone-ware, although it becomes somewhat rounded on the angles, and, as is the case with all earthen crucibles, it acquires a copper-red colour on the surface. Nevertheless, the crucibles of Deyeux are much inferior to those of Beaufay, as they will only retain melted litharge during a very short time. They are made of a mixture of clay and quartz in fine powder.[2] Deyeux and others exhibited collections of crucibles at the Great Exhibition in 1851. In the Report of the Jury, which was drawn up by Dufrénoy,[3] it is stated that "the crucibles manufactured by Deyeux are of two distinct kinds, according to the uses for which they are destined: those intended for fusing bronze, copper, gold, and silver, are marked with the letters [A. D.]; the others, manufactured expressly for the fusion of cast-iron or steel, are marked No. 28." These crucibles, it is further stated in the Report, were introduced about ten years previously; and yet Berthier has described and given an analysis of them in his 'Traité des Essais,' published in 1834.[4] The exhibitors presented favourable testimonials as to their quality from Thénard, D'Arcet, and Despretz. The following analyses of the crucibles of Beaufay and Deyeux are by Berthier.

	Beaufay's.	Deyeux's.
Silica	64·6	72·3
Alumina	34·4	19·5
Sesquioxide of iron	1·0	3·9
Water	..	1·8
	100·0	97·5

Some of Deyeux's crucibles, which we have tried, are perfection in shape and excellence of manufacture.

Belgian Crucibles.—M. St. Clair Deville informed me (1856) that all the varieties of crucibles at the Great Exhibition in Paris, 1855, were tested, and that those of Coste (fabricant de creusets réfractaires à Tilleur, près Liège, Belgique) were found to be by far the best.

We have made trial of Coste's small crucibles, with which we were kindly supplied by Mr. Matthey of Hatton Garden, and found no difficulty in melting them, so that they must have been very inferior to those previously examined by Deville.

GRAPHITE, BLACK-LEAD, OR PLUMBAGO CRUCIBLES.—Graphite is carbon in a peculiar allotropic condition. It occurs in various parts of the world in association with igneous and metamorphic rocks; and it is also artificially produced in the smelting of iron. It is neither fused nor in any way changed by exposure to the highest temperatures, provided access of oxygen be prevented; and it is burned with great difficulty even when strongly heated in atmospheric air. On account of these properties it is a valuable material for crucibles. Native graphite varies considerably in purity and state of aggregation. It is unctuous to the touch,

[2] loc. cit. [3] p. 27. [4] 1, p. 68.

and when rubbed between the fingers produces a peculiar mark, which can only be imitated with a few other substances, as, for example, sulphide of molybdenum or tungsten and micaceous iron ore. Graphite suitable to the manufacture of the best blacklead pencils is of rare occurrence, and, consequently, fetches a high price. No graphite has been so much in request for this purpose as that of Borrowdale in Cumberland; but graphite adapted to the manufacture of crucibles may be procured in abundance in various localities at a moderate price. It is the peculiar state of aggregation which gives value to the Borrowdale graphite, and not its purity; for, according to Karsten, it leaves on combustion not less than 13·3 per cent. of ash;[5] whereas some of the Ceylon graphite, which is of comparatively small value, may contain only traces of foreign matter.[6] The specific gravity of the native mineral may vary much even in the same piece. Thus, in different parts of one piece of 8 or 9 cubic inches in content, Karsten found the specific gravity to vary from 2·226 to 2·419, a difference of about 0·2, which corresponds to a difference in the amount of foreign matter, as the two pieces yielded respectively 13·10 and 14·27 per cent. of ash.

COMPOSITION OF GRAPHITE FROM DIFFERENT LOCALITIES.

No.	Locality.	Ash per cent.	Composition of Ash.						
			Silica.	Alumina.	Sesquioxide of Iron.	Lime.	Magnesia.	Oxide of Manganese.	Titanic Acid.
1	Borrowdale.....	13·3	36·5	26·7	18·1	trace	2·7	1·3	14·2?
2	Passau, Bavaria, as it occurs in commerce	58·0	26·4	25·1	6·5	..	..	..	..
3	Do. do.	65·1	41·2	14·7	8·2	..	1·0	..	..
4	Schwarbach, Bohemia, first quality.....	12·5	5·1	6·1	1·2	0·1	..	..	..
5	Hafnerluden, Moravia	57·0	49·2	7·0	0·8	..	..	..	..
6	Kaisersberg.....	57·8	..	..	..	..	..	..	..
7	India, from the Himalaya	28·4	..	..	..	..	..	..	..
8	Ceylon, unpurified	37·2	..	..	..	..	..	..	..
9	Do. coarsely purified	18·5	..	..	..	..	..	..	..
10	Do. crystallized	0·0 to 1·2	..	..	..	..	..	..	..

1. By Karsten, op. cit. It contained also traces of chromium and magnesia. Surely so large a proportion of titanic acid cannot be present in this graphite.—2, 4, 5. By Ragsky, Kenngott, Uebersicht, 1856, p. 119.—3. By Berthier, Tr. des Essais, 1, p. 50. 6. By Ferstl, Jahrb. d. k-k. Geolog. Reichsanstalt, 1854, p. 869.—7–10. By Prinsep.
No. 3 contained a trace of pyrites.

Graphite intended for crucibles is ground and sifted; and the powder is mixed with a sufficient amount of refractory clay to render it plastic, as it possesses no plasticity of itself. The well-known crucibles of Passau are said to be made of a mixture of 1 part of clay from

[5] Archiv, 1st Ser. 12, p. 93.
[6] Dumas and Stas. Ann. de Chimie et de Phys. 3rd ser. 1, p. 26.

Schildorf and from 2 to 3 parts of an impure graphite which occurs in gneiss in that locality.[7]

Good black-lead crucibles may be characterised by the following properties: they support, even when of the largest size, the greatest and most sudden alternations of temperature without cracking; they may be used after repeated heating and cooling, so long as they are not too much reduced in thickness by the burning away of the graphite to bear the weight of the metal which may be melted in them and to admit of being held by tongs without breaking; their surface within as well as without may be made very smooth, so that particles of melted metal will not hang about the sides; an advantage not possessed by any other crucibles in the same degree, and much valued in the casting of metal for coining, as it may be poured out perfectly clean or free from particles derived from the crucible:[8] they have, however, the disadvanatge of being expensive. Although the graphite may burn away in a greater or less degree on the surface of a crucible, yet it is pretty well protected by the clay with which it is mixed from the action of any free oxygen which may exist in the gases of the furnace. When these crucibles are kept some hours at very high temperatures, much of the graphite may burn away and the exposed clay be melted into slag. It is usual with some persons, before using black-lead crucibles, to coat them externally by dipping them in a mixture of the consistency of cream, prepared with clay and water, containing borax in solution.

Some years ago I had occasion to employ black-lead crucibles of large size,—capable of holding from 40 to 60 lbs. of metal,—and to subject them during many hours continuously to the highest temperature of air-furnaces, in which nickel could be easily melted by pounds at a time. I found that while some stood perfectly well under these conditions, many were quite worthless. I did not previously coat them with clay, and notwithstanding they resisted well. This difference in quality must be due either to the amount or quality, or both, of the matter associated or mixed with the graphite. Although graphite is of itself infusible, yet the foreign matter with which it is mixed, either naturally or artificially, may become soft and pasty at very high temperatures, and so render the crucible more or less yielding to the tongs. We have found the black-lead crucibles manufactured by Mr. Ruel, of High Holborn, to be of excellent quality, and capable of resisting the highest temperature of our air-furnaces in which we can melt manganese or wrought-iron with facility. I used them with perfect success in numerous experiments on the artificial formation of silicates, which, in many cases, required a very high and long-continued heat. It should be remembered that natural graphite frequently contains a sensible amount of oxide of iron, which may be reduced to the metallic state by heat, so that matters melted or heated in such crucibles may become contaminated with iron. The black-lead crucibles which Mr. Ruel placed in the Great Exhibition of 1851 were reported on very favourably by Mr. Henry, who subjected them to severe tests. "Mr. Ruel," writes Mr. Henry, "has so improved the

[7] Knapp, Lehrbuch d. chemisch. Technologie, 1847, 1, p. 598.

[8] Ibid.

black-lead or plumbago crucibles as to drive the foreigner out of the English market. I have repeatedly tried them, and found them excellent. Messrs. Brown and Wingrove, the gold-melters, use them exclusively."[9] That firm furnished the Jury with the following written opinion of their experience of these crucibles:—They are "the best quality for all the most important purposes for which such utensils are required."

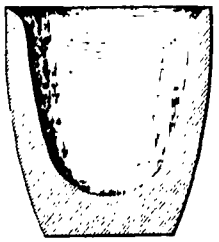

Fig. 62. Section of Juleff's crucibles, to the scale of ½.

Of late we have employed black-lead crucibles manufactured by the Patent Plumbago Crucible Company at Battersea, and have found them in quality equal to those of Mr. Ruel. Of the black-lead crucibles manufactured on the Continent, those of Passau have long been highly esteemed. At the Great Exhibition of 1851 the firm of Messrs. Lorenz, Kapeller, and Son, of Hafnerzell, near Passau, exhibited a series of these crucibles, which were reported to be highly refractory; they were well made, and one was unusually large, being 2 feet high and 20 inches wide. Annexed is the section of a plumbago crucible manufactured for tin-assayers by Juleff of Redruth.

Mould for making very small Crucibles.—More than ten years ago Mr. Rinmann, of Sweden, presented me with a mould which he informs me was employed in Sweden for making small crucibles used in assaying iron-ores.[1] Ever since we have employed crucibles of this kind with great advantage, not only in assaying iron-ores, but also in metallurgical experiments of various kinds. A description of the mould has appeared in Swedish, and more recently in German. The following description of it includes certain alterations in details, which Mr. Smith, in the course of long practice in our assay-laboratory, has found it expedient to adopt. Fig. 63 is a vertical section through the centre; fig. 64 is a horizontal section on the line A B, fig. 63; and fig. 65 is an elevation of the part *f*, seen in section in figs. 63 and 64. All the figures are drawn to a scale of ½. *a* is a short hollow slightly conical piece, open at both ends, made of gun-metal. *b b* are short

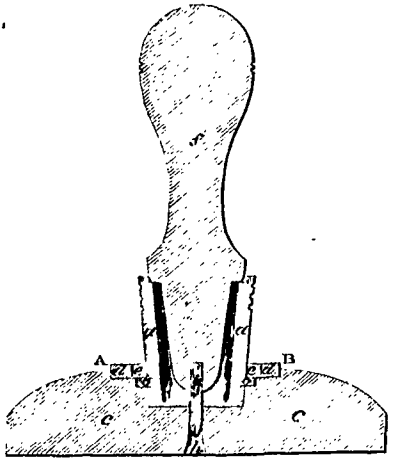

Fig. 63.

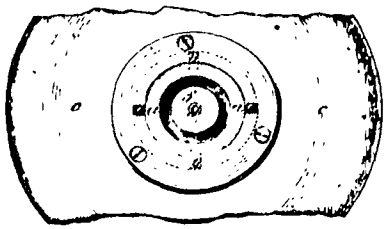

Fig. 64.

[9] Jury Reports, p. 585.
[1] It is described and figured in the Jern-kontorets Annaler, 1852, p. 56.

pins of iron inserted one in each side of *a*, near the bottom or narrower end. *c* is a round block of wood, in the centre of which, on the upper surface, is a circular cavity large enough to receive the lower end of *a*, including the projecting pins, *b b*; through the middle of this cavity is a hole, *h*, and upon the bottom lies a disc of gun-metal, as seen in fig. 63, which also has a hole in the centre of the same size as *h*. Around the edge of this cavity is screwed a flat ring of brass, *d d*, which projects inwards to the extent shown by the dotted line in fig. 64. *c c* are notches to allow the pins, *b b*, to pass through, so that *a* may be turned in the position seen in fig. 64, when the pins, *b b*, will hold it firmly under the projecting edge of the ring of brass. *f* is a circular wooden plug, in the bottom of which is fixed the iron pin, *g*; by means of this pin the plug is kept upright exactly in the centre of the mould. Fig. 65 is another wooden plug, without a pin, but having an oblique groove, *i*. The inner surface of *a* is very slightly oiled, and also the outer surface of *f*, where it passes into *a*. *a* being adjusted, as shown in fig. 64, a small lump of *well-tempered* clay is put into *a*, when the plug, *f*, is forced down and turned round; the excess of clay escapes from the upper edge of *a*; *f* is now withdrawn, and a small bit of clay is dropped in, when *f'*, fig. 65, is forced down and turned round and round; the excess of clay escapes by the groove, *i*. *f'* is then taken out, and *a*, with the contained crucible, detached. The crucible may be removed by being pushed gently upwards with a circular piece of metal or wood applied to the bottom. The mixture we usually employ consists of raw and burnt clay (the latter being obtained by simply burning the raw clay), in the proportion of about 2 measures of unburnt to 1 measure of burnt clay. The crucibles are burnt in a muffle before they are used.

Fig. 65.

Lining Crucibles with Carbon.—This is done when it is necessary to protect the crucible from the corrosive action of matter which may be heated in it, or when a small quantity of a metallic compound is reduced, of which every particle of the metal must be collected, as in the assaying of iron-ores in the little crucibles just described, when not more than 10 grains of ore are operated upon at a time. The minutest portions, which may become entangled in the lining, may be separated by gently crumbling it to powder and applying the magnet. In the case of a difficultly-reducible oxide, like protoxide of manganese, the oxide would powerfully corrode an earthen crucible at a temperature far below that at which reduction occurs; but a carbonaceous lining would effectually prevent contact between the oxide and the sides of the crucible. The atmosphere of a crucible so lined will always be *reducing* at a high temperature, owing to the *carbonic oxide* which must always be present. When the lining is sufficiently thick, it may not even be necessary, in certain cases, to mix the oxide intended to be reduced with carbon. Such a lining may tend to prevent the crucible from sinking down upon itself when softened by an intense heat and exposed to the weight of the fuel. Various

kinds of carbonaceous matter may be employed, according to circumstances. In the case of very small crucibles, charcoal powder, mixed with sufficient gum-water, starch, paste, or treacle, just to make it adhere together by pressure, should be gently rammed in so as entirely to fill the crucible. A cavity may then be made in the charcoal by boring with an instrument like fig. 66, and the surface of the cavity so made may be afterwards rendered perfectly even and smooth by pressing down the instrument, fig. 67, and turning it round. A section of a crucible thus prepared is represented in fig. 68. The diameter of the cavity should gradually diminish from top to bottom. For some time we used lamp-black, which has the advantage of being easily and solidly compressible without any addition; but we abandoned it on account of the impurity of the commercial article, which contains sulphates. The charcoal lining answers perfectly: we have occasionally replaced it by little crucibles of charcoal from a solid wood like box or ebony. Large crucibles may be coated internally with the same mixture of charcoal as is used in the small ones; but a mixture of anthracite powder, or the powder of gas-retort carbon, and gas-tar answers still better. The carbon crucible, for such is the lining, may be conveniently made in a separate mould, and afterwards carefully dried, then imbedded in anthracite powder or coke-dust in a closed iron box, and exposed to a red heat. The box should have an overlapping lid, and, after heating, should not be opened until the contents are cold. When gas-retort carbon is used, a vessel may be obtained in this way which, when struck, yields a sonorous ring like pot or metal. One of these vessels may be dropped into a clay crucible just large enough to receive it, and, when properly treated, it may be used more than once. A carbonaceous lining is, as has been previously mentioned, termed *brasque* by the French, who employ the verb *brasquer* to express the lining of a crucible with carbon. As the words are short, and often used in English, they will be adopted in this work.

Fig. 66.

Fig. 67.

Fig. 68.

To the scale of ¼.
The boring parts are made of gun-metal.

Covers of Crucibles.—When necessary, the mouth of the crucible may be fitted with a cover, made of the same materials as the crucible. Such covers may be easily made by cutting or stamping them out of the clay mixture rolled out upon a flat surface. Pieces of old crucible or thin fire-bricks, termed *split-bricks*, may also be conveniently used for the same purpose. Sometimes it is desirable to lute on the cover with clay. In the case of small crucibles a bit of old crucible may be stuck into the mouth and plastered over with clay. For the small crucibles prepared in the mould, of which a description has been given, we are accustomed to make nicely-fitting covers in a mould of the following construction, and which is shown in the annexed woodcut in vertical

section through the centre. *a* is a cylindrical piece of wood, upon which is placed a cylinder of brass, *b b*, perforated with several holes, *c c*, &c.; *d*, a cylindrical plug of wood hollowed out at the bottom, as represented in the woodcut. This plug fits into the brass cylinder, *b b*, upon the top of which it is supported by a shoulder, so as to leave a space, *e*. A small lump of clay being put into the cylinder, the plug *d* is pressed down and turned round, when a cover is moulded in the space *e*, the excess of clay being expelled through the holes, *c c*, &c. The plug is first withdrawn, and then the cylinder, after which the cover, which is formed with the top or flat side downwards, may be detached and left in a warm place to dry.

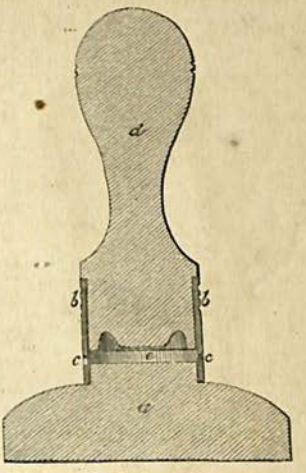

Fig. 69. Mould for making covers, to the scale of ¼.

Crucible stands.—When crucibles are heated in a common air-furnace, it is desirable to support them on a stand about 2 or 3 inches above the bars. Supports of refractory clay are sometimes expressly made, but bits of fire-brick, chipped to a convenient shape and size, answer perfectly.

Tongs for Crucibles.—The annexed engravings are taken from photographs of various kinds of tongs for manipulating with crucibles. They are made of iron. Fig. 70, adapted for small crucibles. Fig. 71, used by the Cornish copper-assayer: the ends consist of rectangular pieces of iron. Fig. 72, of general utility; but as the leverage is great, they must be used with care. Fig. 73, for large crucibles, such as are used by brass-founders. When these tongs are employed to take out of the furnace a large crucible containing a heavy weight of metal, it is customary to slide an iron ring over the handles, in order to prevent the crucible from slipping through.

Scale of 1½ inch to 20 inches.

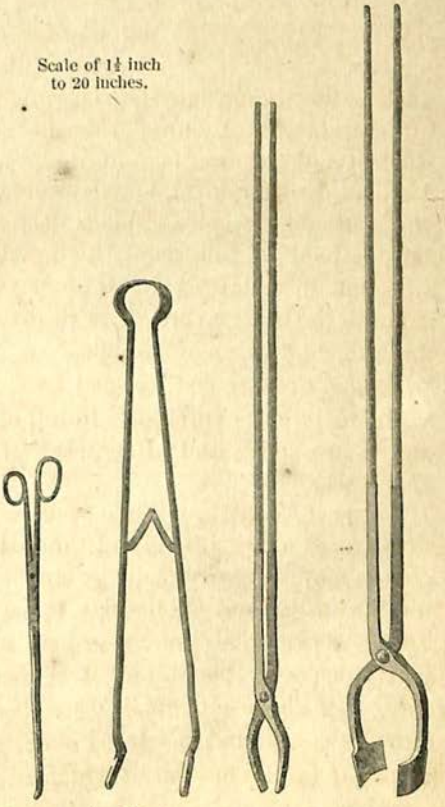
Fig. 70. Fig. 71. Fig. 72. Fig. 73.

Sefström's blast furnace.—For this useful furnace we are indebted to Sefström, the well-known Swedish metallurgist. It is extremely convenient for

easily and rapidly producing high temperatures. It may be made very portable, and at a cost only of a few shillings. The annexed woodcut represents a vertical section through the centre of a small furnace of this kind, in which the crucibles described at page 228 are heated. During many years I have employed this furnace with great advantage in various metallurgical experiments, and I can confidently recommend it to persons who may travel in distant parts and desire to take with them a furnace not exceeding the size of a hat. It is cylindrical, and is made of sheet-iron; and consists of an outer cylinder *a a*, closed at the bottom except at *f*, where a short pipe is inserted for the entrance of the blast; and of an inner cylinder *b b*, completely closed at the bottom, and fixed in the position shown in the woodcut by a rim *g g*. There is thus formed a hollow space or chamber *c c c*, into which air can be blown through the orifice *f*. In the inner cylinder *b b*, are eight small holes *e e e*, at the same height from the bottom, and at equidistant spaces. Into each of these holes is inserted a small nozzle of sheet-iron tapering inwards. The interior of the inner cylinder is lined with a suitable mixture of fire clay *d d*, which is represented by the shading of sectional lines. Any cracks which may occur during the drying of the clay must be filled up with the clay mixture, so that the lining may be rendered compact. It will be observed that the inner cylinder projects somewhat above the rim *g g*. Round this projecting part a hoop of sheet-iron, *h h*, is dropped so as to rest on the rim *g g*, by which means the furnace may be heightened, and space provided in which fuel may be piled. The hoop *h* is formed by bending the sheet-iron and overlapping the ends, in one of which there are two small holes, *i i*, while in the other is fixed a button, which may be fitted at pleasure into either of the holes. The diameter of the hoop may thus be made greater or less, so as to be placed either round the top of the inner cylinder above *g g*, or, when the furnace is not in use, round the outer cylinder *a a*. Charcoal is the fuel usually employed, and it should be reduced to pieces about as large as walnuts. A small pair of double bellows is required to produce the blast. Four of the small iron-assay crucibles of Ekman, or even more, may be heated at a time in this furnace. Sefström's furnaces may be made of much larger dimensions when portability is not an object.

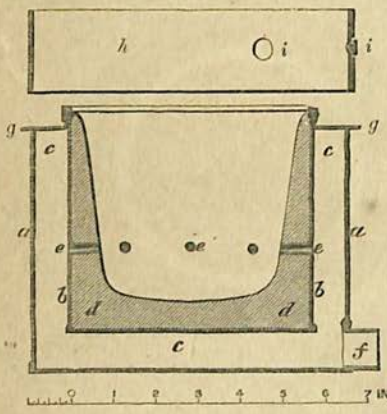

Fig. 74. Vertical section through the middle.

Deville's blast furnace.[2]—In the metallurgical laboratory of the School of Mines we have used this furnace during several years, and find it

[2] Ann. de Chimie et de Phys. 3. s. 46, p. 190. 1856.

very convenient for obtaining high temperatures. Deville has melted platinum in it. Fig. 75 is the plan, and fig. 76 is a vertical section through the centre of fig. 75. A is a vessel of cast-iron, having a circular hole *b*; it is supported by a tripod, of which *d d* are two legs; *a* a circular cast-iron plate, which forms a cover to A; in *a* is a series of holes, *c c*, equidistant from the centre. B is a cylinder of sheet-iron, strengthened at the top and bottom by two rings of iron, *e f*; within it is lined with a mixture of burnt and raw fire-clay to the thickness of the rings, *e f*; any cracks which may be formed during the drying of the clay lining must be filled up. The blast enters at *b*, fig. 76, and rises through the 16 holes in the plate *c*. The crucible is placed on a stand in the centre. The construction of this furnace is such as to produce an intense heat over a wide surface, but within a very limited height from the bottom. Coke, not too dense, of about the size of walnuts, is an excellent fuel for this furnace. Deville uses cinders or "breezes" from the ash-pit of a furnace in which the non-caking coal of Charleroi is burnt; the "breezes" are sifted and thus obtained, varying in size from a pea to a hazel-nut. Ignited charcoal is first introduced to the height of 2 or 3 inches, then pieces of coke of the size of walnuts, and lastly "breezes." According to Deville's experience, at the high temperatures which he obtains, and which he characterises as *blue heat*, the best earthen crucibles become as liquid as glass. He accordingly prepares crucibles of lime, carbon, or alumina. A piece of well-burnt, slightly hydraulic lime, is cut by means of a saw or knife into a rectangular prism with a square base, 3 or 4 inches on the side, and from 5 to 6 inches high. The edges of the prism are roughly rounded off, and a cavity of variable dimensions is bored in the centre. Often in experiments requiring a very high temperature, a small crucible of well-selected lime is enclosed in another lime

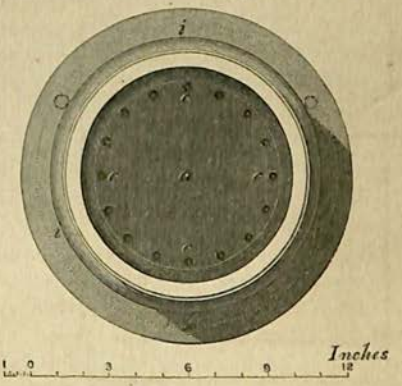

Fig. 75.

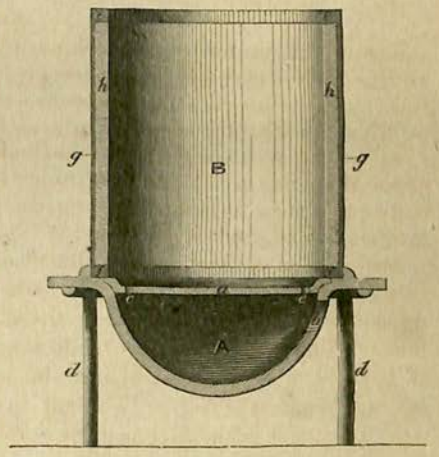

Fig. 76.

crucible. Lime crucibles may be easily and rapidly made. Covers of lime are also employed. When cut in the manner described, no stands are necessary for these crucibles. When the substance to be heated is very refractory, only one crucible is used, of the dimensions above prescribed for the outer one; and the diameter of the cavity should at the most not exceed $\frac{3}{4}$ or $1\frac{1}{4}$ inch, so that the thickness of the walls may remain from about $1\frac{1}{4}$ to $1\frac{1}{2}$ inch. The thickness of the bottom should be from 2 to $2\frac{3}{8}$ inches. The temperature should be gradually raised; and before the "breezes" are put in, care should be taken to ascertain that the lime crucible is not cracked.

The carbon crucibles which Deville employs are turned in a lathe out of gas-retort carbon. They should be perfectly cylindrical, and never exceed the height of 4 inches, inclusive of the thickness of the bottom, whatever may be their width. The reason assigned for this is that the zone of maximum temperature in Deville's furnace hardly extends to the height of $3\frac{1}{4}$ inches. These crucibles may be freed, at least to a certain depth below the surface, from impurities, such as sulphur, iron, silica, and alumina, by exposing them, along with their covers, in earthen crucibles, through the bottom of which a current of chlorine is introduced. The carbon often loses sensibly in weight by this process, but keeps its solidity. When used, a carbon crucible is placed in another crucible of lime or refractory clay, and the space between the two is filled with powder of alumina, which has been previously exposed to a white heat. A cover of gas-retort carbon is placed on the carbon crucible, and over the cover powder of alumina is spread and pressed strongly down. Upon the whole is placed a clay cover. During the process of heating the outer covering may melt completely, yet the carbon crucible within will remain protected by the alumina, which the clinker of the fuel will scarcely attack.

Alumina crucibles are made of a mixture of gelatinous alumina mixed with a proper proportion of alumina which has been previously heated very strongly during a long time. Deville prefers alumina made at a very low temperature from ammoniacal alum, as it forms a plastic mixture with water, and it is very difficult to triturate the lumps in ordinary gelatinous alumina. Instead of calcined alumina, Deville uses the powder of the product obtained by exposing an intimate mixture of equal parts of alumina and pounded marble to the highest temperature of a good air-furnace. It is often scoriaceous and translucent, and resembles dried flour paste. With equal parts of plastic alumina, calcined alumina, and the product last described, or the so-called aluminate of lime, crucibles may be prepared which soften a little at the temperature of melted platinum, but which, by being strongly heated, acquire a remarkable degree of solidity. For very high temperatures less aluminate should be added; but it is desirable that the mixture should contain from 5 to 10 per cent. of lime. Deville remarks that however these crucibles may be made, when once baked they will stand every test. They resist sudden and great changes of temperature, and almost every kind of matter, even sodium, which may be heated in them.

Fire-bricks.—The term *fire-brick* is applied to bricks capable of resisting high temperatures, whether made of natural fire-clay or other refractory matters. They are only used in those parts of furnaces where the heat would be sufficient speedily to destroy ordinary bricks, the use of which is therefore restricted to the external or cooler parts. They are made of varying shapes and sizes to suit the manifold requirements of the furnace-builder. In large establishments, such as the iron-works of South Wales, they are made on the spot. Much of what has been previously stated concerning crucibles will equally apply to fire-bricks. They are made of raw clay ground between rolls or under edge stones, and suitably kneaded by treading after the addition of water. They are fashioned by hand in moulds similar to those used in the manufacture of common bricks.. They are carefully dried in stoves, and burnt at a high temperature in closed kilns. In some establishments the powder of burnt clay is used in admixture with raw clay. The tenacity of a clay must be much affected by the amount of *free* silica which it contains: when it is naturally too tenacious to admit of being directly applied, the right *temper* may be readily produced by the addition of a proper amount of burnt clay in coarse powder. In setting fire-bricks, fire-clay should be used instead of lime-mortar.

The qualities which may be required in fire-bricks are as follow:—

a. They should not melt or soften in a sensible degree by exposure to intense heat long and uninterruptedly continued.

b. They should resist sudden and great extremes of heat.

c. They should support considerable pressure at high temperatures without crumbling.

d. They may be required to withstand, as far as practicable, the corrosive action of slags rich in protoxide of iron.

Experiment on the large scale is essential to the formation of a correct judgment as to some of the qualities which may be required. External characters alone will not suffice.

Stourbridge bricks have long been highly valued for their refractory qualities, and they have been exported to various parts of the world, even far remote. Excellent fire-bricks are also manufactured in many parts of the United Kingdom with clay from the coal-measures. All these bricks have a pale-brownish colour. Sometimes they are copiously mottled with dark spots, due, I believe, to the existence of particles of iron-pyrites diffused through the clay.

Brongniart mentions several kinds of French fire-bricks as being in the highest degree refractory, namely, those from *Mouchy*, Saint Eloy (Oise), manufactured by Deyeux; those from *Septveille*, near Provins; and those from *Saint Vallier*, near Oriol. He states that all these bricks were exposed to the highest temperature of a porcelain-furnace, but protected from the direct action of the potash contained in the ashes, —wood being the fuel,—and that they suffered no change; whereas, Stourbridge bricks exposed to exactly the same conditions became red-brown, and were completely softened.[3]

[3] Traité des Arts Céramiques, 1, p. 341. 1844.

In the following short table is presented the composition of fire-bricks from different localities:—

Composition of various Fire-Bricks.

	1.	2.	3.	4.	5.	6.	7.
Silica	63·09	84·65	88·1	84·0	88·43	69·3	77·6
Alumina	29·09	8·85	4·5	14·1	6·90	28·5	19·0
Lime	0·42	1·90	1·2	0·7	3·40	..	..
Magnesia	0·66	0·35	..	..	trace.	..	2·8
Sesquioxide of iron	2·88	4·25	6·1	0·5	1·50	2·0	0·3
Potash	1·92	..	..	..	..	..	..
Soda	0·31	..	..	..	..	..	..
Titanic acid	2·21	..	..	..	..	..	..
	100·58	100·00	99·9	99·3	100·23	99·8	99·7

1. Communicated to the Author.—2. Richardson, Knapp's Technology, Trans. 2, p. 481.—3. 4. 5. Napier, Phil. Magazine, 4 s. 4, p. 348.—6. 7. By Berthier, Traité des Essais, 1, p. 67.

1. By Riley. This analysis, I am informed, was made with *extreme* care. The clay from which the brick was made is known as the *little vein west clay*, Dowlais. 2. From Windsor clay, which is stated to be a mixture of 70 per cent. of sand and 30 of clay. 3. From Flintshire. This brick is stated to be used in the construction of furnaces and chimneys in the copper-works of Wales in parts exposed to great heat and currents of air; but not where melted matter can come in contact with it. 4. From Lysnewydd, S. Wales: it is used for fireplaces and hearths. 5. From Pembroke: it is used in copper-works. The analysis is by Cameron, late of the Spitty Works. 6. From Creusot, France: it is used for blast-furnaces. 7. From Provins, France: it is used in reverberatory furnaces.

Dinas fire-brick.—This brick consists almost entirely of silica. It was invented by the late Mr. W. Weston Young, a land-surveyor, of Newton Nottage, Glamorganshire, whose original documents on the subject have been placed at my disposal by his great-nephew, Mr. Edward Young. A company was established for the manufacture of these bricks in 1822 by Mr. Young, who thus describes the history of his invention:—"The material at the Dinas (the well-known rock of that name in the Vale of Neath), from which we procure it, is nearly pure silex; but, from its lying on the limestone and occasionally intermixing with it, there is, taking the average of the general working, perhaps, about 5 per cent. of calcareous matter and 1 per cent. of metallic, either iron or copper. Its use as a sand was discovered about 40 years ago,[4] when the fine of it was taken to one of the copper-works and used as a cement, and for mending their furnaces while at work, by placing it with a long iron-handled ladle or spade where the wash of the metal had destroyed the brick; and, from its remarkable property of swelling in high heats, it fixed itself firmly. It gradually

[4] The description is not dated, but it was written 12 years after the bricks had come into use.

gained from one copper-work to another till its use became general: in fact, they are not able to find any other sand that will answer the purpose so well. Its fire-proof qualities being known, many attempts were made to produce a brick from it; but all the common combinations of different clays, &c., failed. About 14 years ago I became acquainted with it, and soon after devised a method of producing a brick from it of very extraordinary fire-proof qualities. When set in its own cement, for very high and long-continued heats it certainly will exceed in duration any other known brick. It does not suit every situation, as, in fact, no fire-brick will: the nature of it at once tells you it must not be placed near alkaline substances; neither will the effluvia from some lead ores suit it. Perhaps it does not exceed Stourbridge (brick) for grates; but for the body of furnaces of most kinds it exceeds, as said before, that and every other known brick in duration. The manner in which the brick is made gives it a rough coat compared with most others; indeed, it is peculiar in this respect; but, as it is made in machines perfectly square, all the works here prefer it with its rough coat; they say it sits better in the work, and they have now had more than 12 years' experience. This brick ought to be kept dry if possible, for, being open in its texture, it imbibes moisture freely." . . . . . "The fire-place, roofs, sides, and bridge of the furnace, also the lower part of the stack, should be built of Dinas; the back part and the remainder of the stack will do best of the other kind (similar to Stourbridge in quality); slabs for leaving the flues and doors are also best made of this material. The appearance of the Dinas brick is peculiar in colour and the roughness of its surface."

The mode of making the Dinas brick was long kept rigidly secret, and even now it is not generally known. The material, which is called "clay," is found at several places in the Vale of Neath, some of which I visited with Mr. E. Young (1859). It occurs in the state of rock and disintegrated like sand. Its colour, when dry, is pale grey. The rock, when not too hard, is crushed to coarse powder between iron rolls. By exposure to the air the hard rock becomes somewhat softer, but some of it is so hard that it cannot be employed. The composition of Dinas "clay," from two localities in the Vale of Neath, is stated in the following table. The analyses were made in my laboratory by Mr. W. Weston. No. 1 was rock of medium hardness, which I obtained near Pont Neath Vaughan, on the occasion of my visit with Mr. E. Young; and No. 2 was sent to me from the same locality, though not from the same mine.

	1.	2.
Silica	98·31	96·73
Alumina	0·72	1·39
Protoxide of iron	0·18	0·48
Lime	0 22	0·19
Potass and soda	0·14	0·20
Water combined	0·35	0·50
	99·92	99·49

The powder of the rock is mixed with about 1 per cent. of lime and sufficient water to make it cohere slightly by pressure. This mixture

is pressed into iron moulds, of which two are fixed under one press, side by side. The mould, which is open at the top and bottom, like ordinary brick-moulds, is closed below by a moveable iron plate, and above by another plate of iron, which fits in like a piston, and is connected with a lever. The machine being adjusted, the coarse mixture is put into the moulds by a workman, whose hands are protected by stout gloves, as the sharp edges of the fragments would otherwise wound them: the piston is then pressed down, after which the moveable bed of iron on which the brick is formed is lowered and taken away with the brick upon it, as it is not sufficiently solid to admit of being carried in the usual manner. The bricks are dried on these plates upon floors warmed by flues passing underneath; and when dry they are piled in a circular closed kiln covered with a dome, similar to kilns in which common fire-bricks are burned. About 7 days of hard firing are required for these bricks, and about the same time for the cooling of the kiln. One kiln contains 32,000 bricks, and consumes 40 tons of coal, half free-burning and half binding. The price (1859) is 60*s.* the thousand. They are manufactured of various shapes and sizes, to suit the furnace-builder.

The fractured surface of one of these bricks presents the appearance of coarse irregular white particles of quartz, surrounded by a small quantity of light-brownish yellow matter. The lime which is added exerts a fluxing action on the surface of the fragments of quartz, and so causes them to agglutinate. These bricks expand by heat, whereas bricks made of fire-clay contract. On this account they are stated to be advantageous for the roofs of reverberatory furnaces, and in all parts where a solid and compact lining is needed. From their siliceous nature it is obvious that they should not be exposed to the action of slags rich in metallic oxides.

Sand and sandstones.—Silica is extensively used by the metallurgist, both in the state of sand and sandstone. The beds of the reverberatory furnaces in which the operations of smelting and refining are effected in the copper-works at Swansea are made of sand. Great accumulations of blown sand occur on various parts of the neighbouring coast suitable for this purpose; and some of the best quality, I am informed, is met with at Briton-Ferry, near Neath. I received from Mr. F. F. Bankart, late of the Briton-Ferry Copper Works, a sample of this sand, which has been analysed in my laboratory by Mr. W. Weston. It has a brownish-yellow colour, and contains minute fragments of shells. Le Play has also determined the composition of similar sand from Swansea. The analyses are as follow:—

	Weston.	Le Play.
Silica	87·87	86·0
Alumina	2·13	1·6
Sesquioxide of iron	2·72	1·2
Lime	3·79	5·7
Magnesia	0·21	0·8
Carbonic acid and a little water	2·60	4 5
	99·32	99·8

These results show that the composition of the sand is more uniform than might have been expected, as the sample on which Weston operated was obtained (1859) more than ten years after Le Play's. No sensible amount of chloride was detected. The presence of lime is, doubtless, important, by tending to cement the particles of sand together into a more or less compact mass.

M. Kampmann has given the following analyses of sands employed for moulds in various foundries :[5]—

	1.	2.	3.	4.
Silica	92·083	91·907	92·913	90·625
Oxide of iron	2·498	2·177	1·249	2·708
Alumina	5·415	5·683	5·850	6·667
Lime	traces.	0·415	traces.	traces.
	99·996	100·182	100·012	100·000

1. Sand from the foundry of M. Freund at Charlottenburg. 2. Sand employed at Paris for bronzes. 3. Sand from Manchester. 4. Sand from the establishment of Lagua near Stromberg.

According to M. Kampmann, a good sand for moulds may be artificially made from the following mixture :—

Fine quartzose sand	93
Red English ochre	2
Aluminous earth the least possible calcareous	5

In the Museum of Practical Geology is a very fine iron casting which was exhibited at the Paris Exhibition in 1855. It is a circular disc, 40 inches in diameter, and about $\frac{3}{16}$ of an inch in thickness, presenting a pattern of elegant perforated tracery-work; its surface is remarkably smooth, and the casting is sharp and even: it was produced at the works of Count Stolberg-Wernigerode, at Ilsenberg, in the Harz Mountains. The sand which adhered to the surface of the casting as it came from the mould was purposely left attached, and of this a portion was taken for the analysis, which was made in my laboratory by Mr. J. Spiller.

Silica	79·02
Alumina	13·72
Protoxide of iron	2·40
Oxide of copper (CuO)	trace.
Magnesia	0·71
Potass	4·58
	100·43

This sand is stated to consist of three different kinds of material, namely, common argillaceous sand, sand found in diluvial deposits, and sand from solid sandstone. As the first two contain clay, they are carefully heated to dehydrate the clay. The sandstone is pounded under a hammer, and mixed with an equal weight of each of the other

[5] Ann. d. Mines, 4, s. 8, p. 689.

two kinds of sand. The mixture is ground by iron balls in a revolving drum, and afterwards passed through a woollen cylinder, which moves up and down; it is thus obtained in the state of the finest flour, which in moulding may be made to receive the most delicate impress. The moulds used in making the so-called "lace-castings" of cast-iron are also prepared with this flour of sand, the patterns being formed of stamped and perforated paper. A valuable casting-sand is obtained from the New Red Sandstone at Birmingham. There is a quarry of this sand at the old Cemetery, the value of which one of the Directors of the Company some years ago informed me was estimated at not less than 20,000*l*.

Blue bricks.—These bricks, which receive their name from the dark grey glaze on their surface, are made of brick-earth in moulds of the usual kind. They are fired in closed kilns, having been previously dusted over with "iron-scurf," the substance produced by the wear of the siliceous grind-stones employed in grinding gun-barrels, etc., and which consists of an intimate mixture of fine particles of stone and iron. In firing the iron becomes oxidized, and combines with the silica to form silicate of protoxide of iron; and it is this compound which forms the glaze. They are much prized by engineers for special purposes. They are not refractory; but I mention them as the mode of glazing may be interesting to the metallurgist.

There are many natural mineral substances, such as those constituting igneous and metamorphic rocks, which are used in the construction of furnaces, and which I shall not particularly describe in this place, though I shall be careful to specify them in the sequel.

COPPER.

History.—Copper was in use in the earliest times of which any record exists. The ancients obtained it from various localities, amongst which was the island of Cyprus, where, according to Pliny, the metal was first discovered. The copper from this island was known in the Roman market as *æs Cyprium* or *Cyprian* copper.[1] The adjective Cyprium, at first only used to express locality, became corrupted into the substantive cuprum, which replaced the original name, æs; and from cuprum the English word copper is derived.

Colour.—It is distinguished by its red colour from all other metals, or metallic compounds, except that of titanium, which frequently occurs in iron-smelting furnaces. *Lustre.*—It is capable of receiving a very brilliant polish. *Crystalline system.*—It crystallizes in the regular system; and after fusion it may occasionally be obtained in imperfect skeleton or solid octahedrons of considerable size. *Malleability and ductility.*—It possesses these qualities in a high degree. It may be rolled into very thin sheets, beaten out into leaves, and drawn into fine wire. By cold rolling or hammering it becomes hard; but its malleability is restored by annealing at a red heat. It is immaterial whether the heated copper be cooled rapidly or slowly in the annealing process. *Tenacity.*—According to Sickingen, a wire $0^{m}\cdot00216$ (0·0864 in.) in diameter supports a weight of $151^{kil.}$ (332·9 lbs.) without breaking;[2] whereas it is stated by Berthier that a wire $0^{m}\cdot002$ (0·08 in.) in diameter breaks under a weight of $137^{kil.}4$ (302·9 lbs.).[3] Results of this kind are not of much value unless accompanied with precise information as to the degree of purity of the copper, the particular method of its preparation, and the exact conditions, as to temperature, &c., under which they were obtained. *Specific heat* 0·09515, between 0° C. and 100° C. (Regnault). *Linear dilatation by heat.*—The published results do not closely agree. According to Troughton, the co-efficient of linear dilatation for copper wire is 0·000019188, that is, the degree of dilatation of a unit of length for 1° C. *Action of heat.*—It melts at a lower temperature than gold, and at a higher temperature than silver; or, according to Pouillet's estimation of the melting-points of those metals, between 1200° and 1000° C. Before the oxyhydrogen blow-pipe it may be volatilized with facility. It is not sensibly volatilized in close vessels at the high temperature of a porcelain furnace: thus Berthier exposed a known weight of copper in a brasqued crucible to the heat of the furnace at Sèvres during the whole period of one firing, and found that at the most the loss did not exceed $\frac{1}{2}$ per cent. At a temperature below, yet bordering on, its melting-

[1] Nat. Hist., L. xxxiv. cap. i. ii. Sillig. 1851.

[2] Berzelius, Tr. de Chimie, 1846, 2, p. 519.

[3] Tr. des Essais, 2, p. 395.

point, it becomes so brittle that it may be readily reduced to powder by trituration. It is usual in foundries to break ingots of copper in pieces while thus heated. The fractured surface of an ingot broken while strongly heated is coarsely fibrous or columnar; and amongst the fibres I think I have perceived imperfect octahedrons. When comparatively pure copper is melted and poured into a mould without exposure to oxygen, the upper surface sinks in considerably on cooling, and a sound ingot is obtained. However, according to Karsten,[1] the surface of pure copper rises in the mould during solidification after fusion: this point will be fully discussed hereafter.

Atomic weight. 31·648.

Action of oxygen.—There are two oxides of copper, a knowledge of which is important to the metallurgist, namely, the red, or dioxide, and the black, or protoxide. At the ordinary temperature of the air copper is not acted upon either by dry or moist oxygen; but when exposed to moist oxygen and carbonic acid, its surface becomes coated with a green rust of carbonate of copper, commonly, but erroneously, called verdigris, which is acetate of copper. When copper is heated to redness with access of air, its surface is converted into dark-coloured oxide, or copper scale, which may be more or less perfectly detached by plunging the copper while hot into cold water, or by bending it backwards and forwards after cooling. Sheet copper may soon be completely converted into oxide by alternately removing the scale and reheating. A large quantity of this scale is produced in the process of annealing sheet copper in rolling mills. Although the scale has a superficial dark grey, nearly black colour, yet it consists almost wholly of dioxide of copper; it breaks with a crystalline fracture, and, when in thin laminæ, transmits a beautiful ruby-coloured light. The scale, in the state in which it is detached from the surface of the copper, may be exposed during a long time to a strong red heat in a muffle without passing in sensible proportion to a higher degree of oxidation; but when it is thus heated after having been reduced to powder, it swells up considerably, and is speedily and completely changed into protoxide. When copper in a finely divided state—such as is produced by precipitation from sulphate of copper by iron, or by the reduction of the oxides of copper by hydrogen at a low temperature—is heated with access of air to a degree far below redness, it is rapidly oxidized.

Dioxide of copper. Formula, Cu^2O.—It crystallizes in the regular system. It melts between a bright red and a white heat. It is always formed when copper is heated to redness with access of air, or in contact with protoxide of copper. It is easily reduced at a red heat by hydrogen, carbonic oxide, charcoal, or other carbonaceous matters, and metals having a strong affinity for oxygen, such as iron or zinc. When heated in the state of powder to redness with access of air, it is rapidly converted into protoxide. It is resolved by the action of dilute sulphuric acid into protoxide of copper, which dis-

[1] Sys. 5. p. 257.

solves, and into finely divided metallic copper, which remains. By the action of nitric acid upon dioxide of copper, except when very dilute and cold, nitrate of protoxide is formed. It dissolves in hydrochloric acid and ammonia, and the latter solution, which is colourless, becomes blue by exposure to air. It is used in the arts to communicate a fine ruby colour to glass.

Protoxide of copper. Formula, CuO.—It is this oxide which forms the base in ordinary salts of copper. According to Berthier, it melts at a white heat. It is as easily reduced as the dioxide, and by the same reducing agents. Favre and Mauminé state that when protoxide of copper is exposed to about the melting-point of copper, oxygen is given off in a regular stream, which, having once ceased, will not again occur, though the heat may be increased.[5] In four experiments the loss of oxygen varied from 8·0 to 8·2 per cent. The product, which was melted, was black, and consisted of $2Cu^2O + CuO$. I had long previously found that when protoxide of copper was exposed in a clay crucible to a high temperature in a common assay furnace, it became brown and formed a sintered mass; but I was not sure that the reduction was the simple effect of heat, and thought that probably the partial reduction might have been caused by the gases of the furnace. It dissolves in ammonia, forming a deep blue solution: when ammonia is poured upon it, scarcely any coloration will take place; but the addition of a little carbonate or other salt of ammonia will instantly cause the blue colour to appear.

Dioxide of copper heated with silica.—Berthier prepared silicates of this oxide by heating mixtures of fine quartzose sand and protoxide of copper with sufficient metallic copper to form dioxide.

	Dioxide of Copper per cent.	Silica per cent.
1. $3Cu^2O, SiO^3$	82·3	17·7
2. $3Cu^2O, 2SiO^3$	69·9	30·1
3. Cu^2O, SiO^3	60·7	39·3

1. The product was a homogeneous button, easily detached from the crucible, and had only undergone the commencement of pasty fusion; it was compact, tenacious, red-brown, with a somewhat metallic aspect; its powder was bright red. 2. The product was melted into a button filled with small bubbles; its fracture was uneven, shining, and of a fine deep red violet colour. It must have been very liquid, and had partially traversed the substance of the crucible. 3. The product had the same form as the mixture; it was tenacious and cellular; its fracture was partly dull and partly shining; it must have been strongly softened, but yet not perfectly liquid. A portion of the grains of quartz had risen to the surface. In making experiments of this kind, it is desirable in the first part of the process to employ a comparatively low and long-continued heat.

Experiment by R. Smith:—

$3Cu^2O$ = 1400 grains.
$2SiO^3$ = 600 do.

[5] Jahres-Bericht. Berzelius. 1846, p. 184.

The mixture was heated strongly in a plumbago crucible. The product was fritted, but not melted, and red like dioxide of copper. A few small particles of copper were found on the exterior.

Protoxide of copper heated with silica.—Berthier heated the following mixture of this oxide and silica:

3CuO	=	0·421 gramme.
$4SiO^3$	=	0·579 do.

The product was only semi-fused and blood-red in colour, which proves that the protoxide had been reduced to dioxide.

This experiment has been repeated by R. Smith. The proportions employed were 1160 grains of protoxide of copper and 840 of silica. The mixture was exposed in a fine-grained crucible to a high temperature during two hours. The product was fritted, and very similar in appearance to that obtained by heating a mixture of dioxide of copper and silica. Its upper surface was black, and where it was in contact with the crucible it was orange-coloured. In order to be certain that the gases of the furnace in which the crucible was heated had not contributed to effect the reduction of the protoxide to dioxide, the following experiment was made in a muffle, in which the atmosphere was oxidizing—

3CuO	=	580 grains.
$2SiO^3$	=	440 do.

The materials were intimately mixed, and the mixture was exposed in an uncovered platinum dish to a strong red heat in a muffle during $3\frac{1}{2}$ hours. A sound, such as is produced by the evolution of bubbles of gas from a thick liquid, was perceived during the process. The dish with its contents was left to cool in the muffle. The product was detached in one piece from the platinum; it was somewhat compact, semi-fused, opaque, and brown-red; the upper surface was black and porous. The platinum dish was attacked where it had been in contact with the mass. About half of the product was again exposed during $5\frac{1}{2}$ hours in the same platinum dish in a muffle to a degree of heat approaching whiteness. No perceptible change occurred, except the blackening of the surface of the mass. From the preceding experiments it may be concluded that, under the influence of silica, protoxide of copper is reduced at a high temperature to dioxide.

Dioxide of copper heated with silica and alumina.—The following experiments were made by R. Smith:

1.

$3Cu^2O$	=	1200 grains.
Al^2O^3	=	280 do.
$2SiO^3$	=	520 do.

The mixture was exposed to a high temperature during an hour and a half in a plumbago crucible. The product consisted of a vitreous, porous, dirty orange-red slag, and a button of porous copper weighing 550 grains.

2. The same quantities were used. The mixture was exposed in a fine-grained crucible during more than five hours to the highest temperature attainable in a muffle. The product was fritted; it was sepa-

rated as completely as possible from the adherent substance of the crucible, and exposed in a Cornish crucible placed within another during about an hour to a white heat. The product was perfectly melted except on the upper surface, which was porous; its colour was greenish orange.

3. (By myself)	Cu^2O	=	240 grains.
	Al^2O^3 (containing 43 per cent. of dry alumina)	=	133 do.
	SiO^3 (ground flints)	=	102 do.

The mixture was gradually heated to bright redness in a crucible closed by pieces of earthenware biscuit luted over with clay. The product was well melted, free from bubbles, opaque, and of a red-orange colour.

Berthier made the following experiment:—

$3Cu^2O$	=	60·0
Al^2O^3	=	14·4
$2SiO^3$	=	25·6

The product was compact, free from bubbles, with a slightly conchoidal fracture, very bright (très éclatant), of a fine sealing-wax red colour, opaque, even in the thinnest fragments.

Protoxide of copper heated with silica and alumina.—The experiment was made by R. Smith.

3 CuO	=	120 grains.
Al^2O^3	=	52 do.
$2SiO^3$	=	92 do.

The mixture was heated in a fine-grained crucible in the same furnace, and during the same time, with the crucible in experiment 2, p. 244. The product was melted, compact, and of a greenish-orange colour, like that obtained in experiment 2.

Borates of copper. — The following experiments were made by Berthier:—

1.	Cu^2O	=	17·83 grammes.
	$4BO^3$	=	29·44 do.

The mixture melted easily and became very liquid. The product was compact, very hard and tenacious, opaque, cinnabar-red in colour, and had an uneven, slightly shining fracture. It should consist of 50·7 per cent. of dioxide of copper and 49·3 of boracic acid.

2.	CuO	=	9·91 grammes.
	$2BO^3$	=	14·72 do.

The mixture melted easily without any intumescence. The product was tenacious, opaque, and red-brown in colour, spotted with blue. It contained cavities, in which were brilliant prismatic crystals, some red and others of the finest blue colour. Part of the protoxide of copper must have been reduced to dioxide.

The following experiment was made by R. Smith:—

3.	3CuO	=	240 grains.
	$2BO^3$	=	140 do.

The mixture was heated in an open Cornish crucible in a muffle, and in about 20 minutes fused easily at a red-heat; the product was a dark greenish coloured glass when seen by transmitted light, but it was blue and iridescent on the surface.

Disulphide of copper. Formula, Cu^2S.—Copper has a strong affinity for sulphur. When a mixture of sulphur in powder and copper-turnings is exposed to a red heat, combination takes place with incandescence, and disulphide of copper is formed. It may easily be made on a large scale by dropping pieces of sulphur upon copper heated to bright redness in crucibles, or by heating a mixture of copper scales and sulphur. When thus artificially prepared it is compact, and breaks with a granular, columnar, or more or less conchoidal fracture; it is black, with a bluish-grey tinge, and has a feebly-metallic lustre; it melts at a lower temperature than copper, and when melted does not permeate the crucible like galena; it may easily be reduced to powder by trituration. According to Karsten its specific gravity is 5·9775. It undergoes no change when strongly heated without access of air.

Disulphide of copper heated with other sulphides.—According to Berthier it has a strong tendency to combine with all metallic sulphides. Double sulphides of copper and the alkaline metals are easily obtained by heating mixtures of sulphate of copper and alkaline sulphate in brasqued crucibles. Berthier prepared in this way the two following double sulphides:[6]—

1. Disulphide of copper..... 55 parts.
   Sulphide of barium..... 45 do.

It was compact, fragile, lamellar, of a bright lead-grey colour, and resembled galena.

2. Disulphide of copper ..... 67 parts.
   Sulphide of calcium..... 33 do.

It was bubbly; its fracture was granular and crystalline; it had a bluish, metallic, grey colour, and somewhat resembled sulphide of antimony.

The following experiments on the combination of disulphide of copper with sulphide of iron have been made in my laboratory. Nos. 3 and 5 by W. Baker, and No. 4 by R. Smith.

3. Cu^2S = 1000 grains.
   $2FeS$ = 1109 do.

The mixture was exposed in a covered crucible to a strong red heat, and pieces of sulphur were dropped into the fused mass. When cold the product weighed 2176 grains, showing an increase of 67 grains. It consisted of two distinct layers: an upper one, which had a yellow colour and metallic lustre, resembling native iron pyrites; and a lower

[6] Tr. des Essais, 2, p. 406.

one, resembling protosulphide of iron. The whole was remelted, when sulphur was again added, and mixed with the melted mass by stirring with a stick. The product, which was brittle, was broken when cold. It appeared quite homogeneous; its colour was between brass and bronze-yellow; it contained 29·6 per cent. of sulphur. The formula $Cu^2S + 2FeS$ corresponds to 28·69 per cent. of sulphur.

4. Cu^2S = 320 grains.
   FeS = 176 do.

The mixture was melted in a covered crucible. The product weighed 450 grains, the loss being 46 grains; it had a granular fracture, and a dark bluish grey colour; copper in minute particles was diffused through the mass, and moss or filamentous copper occurred in cavities in the interior; it resembled the kind of regulus called *blue-metal* by the copper-smelters.

5. Cu^2S = 1000 grains.
   $2FeS^2$ (native) = 1513 do.

The mixture was exposed in a crucible, having a luted cover, to a strong red heat during twenty minutes. The product, which resembled that obtained in experiment No. 3, weighed 2160 grains, the loss being 353 grains; it contained 30·39 per cent. of sulphur. If the materials had been perfectly pure, and the bisulphide of iron had been completely reduced to protosulphide, the loss would have amounted to 403 grains.

Disulphide of copper heated with access of air.—When disulphide of copper in the state of fine powder is gradually heated with free access of air to incipient redness, and stirred continually, both elements are oxidized. The sulphur is partly converted into sulphurous acid, which escapes, and partly into sulphuric acid, which remains in combination with protoxide of copper, forming sulphate of that oxide. If the roasting be continued until sulphurous acid ceases to be evolved, and at a temperature insufficient to decompose sulphate of copper, the product will consist of a mixture of that salt and protoxide of copper. If, on the other hand, the temperature be raised to a pretty strong red heat, the sulphate of copper will be decomposed, and the product will consist entirely of protoxide of copper, the sulphuric acid of the sulphate being partly volatilized, and partly resolved into sulphurous acid and oxygen.

Theory of the process of heating disulphide of copper with free access of air, or roasting.—We are indebted to Plattner for valuable and interesting researches on the chemical changes which occur in various roasting processes. He states that he has obtained by experiment the following results concerning the roasting of disulphide of copper.

1. A mixture of sulphurous acid and atmospheric air in the ratio of two volumes to five, dry as well as moist, was passed through a glass tube heated to moderate redness. No sulphuric acid was formed.

2. The experiment was repeated with a spiral coil of fine platinum wire placed in the tube. Sulphuric acid was formed, whether the gaseous mixture were dry or wet. The same result was obtained

when the platinum was replaced by gold or silver in a finely divided state, the metals themselves undergoing no change.

3. *Metallic copper.*—Experiment (1) was repeated with finely divided copper, precipitated by iron, from the solution of a salt of copper. At incipient redness dioxide of copper and sulphate of protoxide were formed. The experiment was not continued till the copper had become completely oxidized. During the process only a slight odour of sulphurous acid could be perceived at the open end of the tube.

4. *Dioxide of copper.*—Experiment (1) was repeated with native red oxide. At incipient redness it was very soon changed into protoxide, and this into sulphate of protoxide. During the process only very little free sulphurous acid passed over.

5. *Protoxide of copper.*—Experiment (1) was repeated with this oxide. At incipient redness it was changed into sulphate of protoxide, and neither sulphurous nor sulphuric acid was perceived at the open end of the tube.

6. Dry sulphurous acid gas was passed over protoxide of copper in a glass tube heated to incipient redness, atmospheric air being completely excluded. When cold the matter in the tube was dirty red. It contained a sensible quantity of sulphate of protoxide of copper, which was dissolved out by water. During the passage of the dry sulphurous acid a sublimate of sulphur appeared near the oxide; and at the open end of the tube neither sulphurous nor sulphuric acid was observed. Plattner obtained this deposit of sulphur by exposing oxide of zinc, protoxide of lead, and sesquioxide of iron to precisely the same conditions. Hence he draws the conclusion that, when sulphurous acid gas is passed over easily reducible metallic oxides at a feeble red heat—atmospheric air being excluded—it is not only converted into sulphuric acid at the expense of the oxygen of the oxides with which it comes in contact, but at the same time it may also by simple contact with red-hot solid bodies be resolved into sulphuric acid and sulphur.

7. Dry sulphurous acid gas, without admixture of atmospheric air, was passed over finely divided copper (prepared by precipitation with iron), heated in a glass tube to incipient redness. The copper glowed more brightly, but without causing any manifest decomposition of the sulphurous acid. After cooling, the copper throughout appeared to retain its characteristic colour; nevertheless, on boiling with distilled water, a small quantity of sulphate of protoxide of copper was dissolved out.

8. Experiment (7) was repeated at a red heat with silica in the state of sand and quite free from iron. At first sulphuric acid was formed, but afterwards sulphurous acid chiefly escaped; sulphur was deposited in the tube. This result is remarkable and important, as showing that, at a red heat, by the mere contact of *inert* bodies in a state of fine division, dry sulphurous acid gas is resolved into sulphuric acid and sulphur.

The following conclusions are drawn from the preceding data:—

1. According to Plattner, when finely divided disulphide of copper is

exposed to the action of the air at nearly a red heat, with frequent stirring, so as to change the position of the particles, sulphurous acid and dioxide of copper are at first produced. 2. The sulphurous acid by contact-action (Exp. 8) is partially converted into sulphuric acid at the expense of the oxygen of the current of atmospheric air; and this sulphuric acid, together with the oxygen of another portion of atmospheric air, immediately exerts an oxidizing action upon the dioxide of copper, and probably also upon any unchanged disulphide present; part of the acid combining with the resulting protoxide of copper to form sulphate of copper, and part being decomposed with the evolution of sulphurous acid. The sulphurous acid thus set free may either be driven off by freshly-formed sulphurous acid, or it may again be converted by contact-action into sulphuric acid in the manner described, at the expense of the oxygen of the current of air, which is continually flowing over the matter in process of roasting. 3. So long as sulphurous acid is formed in sensible quantity the whole of the dioxide of copper cannot be converted into protoxide (Experiment 6). Hence, after the oxidation of the disulphide of copper, the product contains from 20 to 30 per cent. of dioxide of copper, mixed with protoxide and sulphate of protoxide. 4. At a higher temperature the sulphate of protoxide of copper will be decomposed, the sulphuric acid, as has been previously stated, being partially volatilized and partially resolved into sulphurous acid and oxygen: this oxygen, Plattner remarks, may, together with that of the atmospheric air present, convert the remaining dioxide of copper into protoxide. But, it may be asked, will not the sulphuric acid volatilized be reduced by dioxide of copper at this increased temperature with the formation of sulphurous acid and protoxide of copper? If the vapour of water be present, as must always be the case in ordinary roasting operations, it will combine with the anhydrous sulphuric acid which may escape, and produce a white vapour.

Disulphide of copper heated in admixture with dioxide, protoxide, or sulphate of copper.—It may be stated as a general fact, that when disulphide of copper is intimately mixed with one or more of these oxidized compounds of copper, in such proportion that the sulphur and oxygen exist in the ratio in which they are combined in sulphurous acid, and the mixture is heated to the melting-point of copper, the whole of the copper will be reduced to the metallic state, and the whole of the sulphur will be evolved as sulphurous acid. Hence it is easy to conceive how, by the action of air and heat alone, disulphide of copper may be completely reduced. It must first be roasted until the product contains sulphur and oxygen in the ratio above-mentioned, and then the heat must be raised to the melting-point of copper. When the oxygen exceeds this ratio, a proportionate amount of dioxide or protoxide of copper, as the case may be, will remain in the product. Conversely, when the sulphur exceeds this ratio, a proportionate amount of disulphide of copper will remain in the product. The following formulæ express the

results, which will occur under varying relations between the sulphur and oxygen :—

1. $Cu^2S + 2Cu^2O = Cu^6 + SO^2$
2. $Cu^2S + 2CuO = Cu^4 + SO^2$
3. $Cu^2S + 3CuO = Cu^3 + Cu^2O + SO^2$
4. $Cu^2S + 6CuO = 4Cu^2O + SO^2$
5. $Cu^2S + CuO, SO^3 = Cu^3 + 2SO^2$
6. $Cu^2S + 2CuO, SO^3 = 2Cu^2O + 3SO^2$
7. $Cu^2S + 4CuO, SO^3 = 6CuO + 5SO^2$

Most of these reactions have been confirmed by experiment in the metallurgical laboratory by my former pupil, Mr. W. Baker, of Sheffield. It must not, however, be supposed that in experiments of this nature theoretical accuracy can be attained, especially on account of the corrosive action exerted at a high temperature by oxides of copper on the substance of the crucibles employed, and the consequent formation of compounds consisting of silica, alumina, and oxide of copper. Nevertheless, with proper care and experience, results may be obtained which sufficiently approximate to those indicated by theory to demonstrate the practical correctness of the formulæ. It is especially desirable to conduct such experiments at the lowest temperature at which the reactions take place, in order to lessen, as far as practicable, the error arising from the corrosion of the crucibles. Care must also be taken to prevent reduction of the oxidized compounds of copper by the gases of the furnace in which the crucibles are heated. By way of illustration, the following results of actual experiments are presented :—

1. Cu^2S = 1000 grains.
   $2Cu^2O$ = 1796 do.

The button of copper weighed 2301 grains. The theoretical quantity is 2391 grains : difference, 90 grains.

2. Cu^2S = 1000 grains.
   $2CuO$ = 1000 do.

The button of copper weighed 1295 grains. The theoretical quantity is 1596 grains : difference, 300 grains. A thin layer of regulus, like disulphide of copper, adhered to the button.

3. Cu^2S = 500 grains.
   CuO, SO^3 = 500 do.

The button of copper weighed 516 grains. The theoretical quantity is 596 grains : difference, 80 grains.

Copper heated with protoxide of lead.—The following experiments were made in the metallurgical laboratory by Mr. R. Smith :—

1. Cu^4 (granulated) = 320 grains.
   PbO (commercial litharge) = 280 do.

The product was melted, and consisted of slag,[7] and a button of

[7] In the description of all these experiments I have used the word slag to denote that part of the product which was neither *regulus* nor *metal*.

metal weighing 340 grains. The slag was compact, opaque, and red-brown. The button was copper-coloured on the external surface and brittle; its fractured surface was fibrous and greyish red; it contained 308·4 grains, or 90·7 per cent., of copper.

2. Cu^2 (thin turnings) = 320 grains.
   PbO (commercial litharge) = 560 do.

The litharge was placed upon the copper, and the mixture was gradually heated to bright redness. The product was melted, and consisted of slag, and a button of metal weighing 340 grains. The slag on its upper surface was dark grey, and presented acicular crystals confusedly grouped; on fracture it was vitreous, opaque, and red-brown. The button was copper-coloured externally, and cracked under the hammer; its fractured surface was dull lead-grey; it contained 288·8 grains, or 83·18 per cent., of copper.

3. Cu = 320 grains.
   PbO = 1120 do.

The product was melted, and consisted of slag, and a button of metal weighing 321 grains. The slag on its upper surface was dark grey, somewhat metallic in lustre, and presented groups of interlacing acicular crystals; on fracture its colour was red-brown, approaching black, near the upper surface. The button was copper-coloured externally; its fractured surface was granular and dull lead-grey; it contained 233·7 grains, or 72·8 per cent., of copper.

4. Cu = 320 grains.
   2PbO = 2240 do.

The product was melted, and consisted of slag, and a button of metal weighing 392 grains. The slag was similar in appearance to that of No. 3, except that it was somewhat mottled. The button was copper-coloured externally, and more malleable than that of No. 3; its fractured surface was finely fibrous, or silky, and lead-grey. The experiment was repeated with granulated copper, and with similar results, except that the button weighed 373 grains; it contained 203·9 grains, or 54·66 per cent., of copper.

5. Cu = 160 grains.
   3PbO = 1680 do.

The product was melted, and consisted of slag and a button of metal weighing 195 grains. The slag on its upper surface was dark grey and somewhat metallic in lustre; the lower part was vitreous and dark brown. The upper part, or about three-fourths of the whole, was granular, and in places presented crystalline fibres; without lustre; varying in colour from red-brown to greenish yellow-brown, and even black; where in contact with the button it was red; it was translucent in thin slices. The button was composed of two layers; an upper one, hard, fibrous on fracture, and, from its appearance, evidently rich in copper, and a lower one, soft, and resembling lead; it contained 56·9 grains, or 29·2 per cent., of copper.

6. Cu = 64 grains.
   6PbO = 1344 do.

The product was melted, and consisted of slag and a button of metal weighing 86 grains. The slag was vitreous, semi-opaque, and dark brown. The button resembled lead, and presented no appearance of separation into two layers; it contained 10·6 grains, or 12·3 per cent., of copper.

These results agree pretty well with those of Berthier,[8] and show that when copper is heated with litharge it is only oxidized to the degree of dioxide; the same fact is also proved by heating a mixture of dioxide of copper and litharge (vide p. 253). In the six experiments preceding, the differences between the weights of the buttons actually found and those which theory would indicate are respectively as follow (the atomic weight of Cu being taken as 32 and that of lead as 104):—12·75, 0·5, 52·9, 0·5, 29·4, and 0·77 grains. These numbers, with the exception of the third, are not greater than may be expected in experiments of this kind. From the last experiment it appears that when copper is heated with 21 times its own weight of litharge not less than one-sixth of it remains unoxidized.

Copper heated with sulphate of lead.—Experiments by R. Smith.

1. Cu^2 = 320 grains.
   PbO,SO^3 = 760 do.

The reaction is very energetic, but it does not occur below a strong red heat. Sulphurous acid is evolved. The product was a compact, opaque, red-brown slag, black and scoriaceous on the upper surface and orange-coloured at the lower part. Berthier describes the product which he obtained from this mixture as compact, with a shining fracture, opaque, and of a very fine sealing-wax-red colour.

2. Cu = 160 grains.
   PbO,SO^3 = 760 do.

The result was similar to that of the last experiment. The slag was brownish-red, and darker near the upper surface, which was coated with a black film of a somewhat metallic lustre. There were no globules of copper, so that the copper was completely oxidized.

Copper heated with sesquioxide of iron.—Experiments by R. Smith. Finely pounded hæmatite and copper in thin shavings were employed.

1. Cu^2 = 64 grains.
   Fe^2O^3 = 80 do.

The mixture was made as intimate as possible. It was subjected, in a small covered clay crucible, to a high temperature in a muffle during an hour. The contents of the crucible adhered together in a black mass. The copper was oxidized on the surface and very brittle.

2. Cu = 32 grains.
   Fe^2O^3 = 80 do.

3. The result was similar to that of the last experiment.

Copper heated with peroxide of manganese.—Experiments by R. Smith.

1. Cu = 64 grains.
   MnO^2 = 200 do.

2. Cu^2 = 64 grains.
   MnO^2 = 50 do.

[8] Tr. des Essais, 1, p. 385.

The results were similar to those obtained with sesquioxide of iron. According to Berthier the peroxide of manganese is reduced to protoxide. and, by the addition of a little glass, a very fusible slag is formed, which contains dioxide of copper and protoxide of manganese.

Protoxide of copper heated with metallic lead.—Experiments by R. Smith.

1. 2CuO = 800 grains.
   Pb (granulated) = 1040 do.

The mixture melted readily into an opaque, crystalline, black slag, having a semi-metallic lustre. The product should have the formula $Cu^2O + PbO$.

2. 3CuO = 480 grains.
   Pb^2 = 832 do.

The product was melted, and consisted of slag, and a button of metal weighing 460 grains. The slag, which was only partly vitreous, was opaque and reddish-brown. The button was copper-coloured externally, and its fractured surface was dull lead-grey; it contained 330·7 grains, or 71·9 per cent., of copper.

3. CuO = 400 grains.
   Pb = 1040 do.

The product was melted, and consisted of a red-brown slag, and a button of metal weighing 343 grains. The experiment was repeated with half the preceding quantities. The slag was vitreous, and redder in colour than in the first experiment. The button resembled lead, and weighed 180 grains; its fracture was fibrous; it contained 119·7 grains, or 66·5 per cent., of copper.

Dioxide of copper heated with protoxide of lead.—Experiments by R. Smith.

1. Cu^2O = 720 grains.
   PbO = 1120 do.

The mixture melted at a low red heat; it attacked and traversed the substance of the crucible with great rapidity. The product is crystalline and reddish brown-black.

2. Cu^2O = 720 grains.
   2PbO = 2240 do.

The mixture melted as in the last experiment, and the product had nearly the same characters; its upper surface was coated with a black film having a semi-metallic lustre. It follows from these results that dioxide of copper is not in any degree oxidized when heated with protoxide of lead; for, otherwise, metallic lead would have been separated.

Protoxide of copper heated with protoxide of lead.—Experiments by R. Smith.

1. CuO = 400 grains.
   PbO = 1120 do.

The mixture melted into a compact, hard, dull slag; its upper surface was black, crystalline, and metallic in lustre; the colour of its fractured surface varied from brown to black from below upwards.

2. CuO = 200 grains.
   2PbO = 1120 do.

The mixture melted into a crystalline, shining, dark-green slag, much softer than the last, and more resembling fused protoxide of lead in appearance; its upper surface was smooth, black, and semi-metallic in lustre.

Protoxide of copper heated with sulphide of lead.—Experiments by R. Smith. The purest galena was employed.

1. CuO = 400 grains.
   PbS = 1200 do.

The mixture melted with considerable effervescence. The product consisted of a vitreous, opaque, black slag, and a regulus weighing 705 grains; its fractured surface was dark grey and crystalline, resembling fused galena in appearance. The experiment was repeated with half the preceding quantities; the regulus weighed 302 grains, and contained 142·3 grains, or 47·13 per cent., of copper. Berthier describes the slag obtained from this mixture as of a fine red colour.

2. 3CuO = 600 grains.
   2PbS = 1200 do.

The mixture melted with much effervescence. The product consisted of a vitreous, opaque, brownish-red slag, and a purplish lead-grey regulus, weighing 710 grains; a small button of soft lead was attached to the lower part; it contained 504·4 grains, or 71·04 per cent., of copper.

3. 2CuO = 800 grains.
   PbS = 1200 do.

The mixture melted with considerable effervescence. The product consisted of a compact, hard, brittle, opaque, sealing-wax-red coloured slag, and a purplish grey regulus, to the lower part of which a copper-coloured button of metal adhered with great tenacity; the fractured surface of this button was close-grained, dull, and reddish grey; it cracked under the hammer. The regulus and button weighed together 565 grains; the button weighed 307 grains, and contained 299 grains, or 97·4 per cent., of copper.

4. 3CuO = 1000 grains.
   PbS = 1000 do.

The mixture melted, but not with quite so much effervescence as those preceding. The product consisted of a brownish red slag, darker on the upper surface, and a copper-like button of metal weighing 140 grains; it contained 138·6 grains, or 99 per cent., of copper.

5. 4CuO = 800 grains.
   PbS = 600 do.

The mixture melted with slight effervescence. The product consisted of a slag like that of the last experiment, and a copper-like button of metal weighing 162 grains; its fracture was fibrous; it contained 156·7 grains, or 96·7 per cent., of copper.

Dioxide of copper heated with protosulphide of iron and silica.—Experiment by R. Smith.

$3Cu^2O$ = 1296 grains.
3FeS = 786 do.
SiO^3 = 276 do.

These substances were intimately mixed, and the mixture was exposed to a high temperature in a close-grained crucible. The product consisted of a vitreous, opaque, black slag, and a regulus which resembled disulphide of copper in appearance, and weighed 1330 grains. The proportions of the mixture are such, that, supposing the copper to be wholly converted into disulphide, tribasic silicate of protoxide of iron would be formed. Admitting this reaction to have occurred, the regulus should have weighed 1440 grains; and as the difference between this number and that actually obtained is only 110 grains—a difference by no means great, considering the nature of the experiment—it may be concluded that the reaction supposed does take place, at least in a very great degree. This reaction is of much importance in copper-smelting, and may be expressed by the following formula:

$$3Cu^2O + 3FeS + SiO^3 = 3FeO, SiO^3 + 3Cu^2S.$$

The same experiment with the same proportions was repeated in a plumbago crucible. A similar slag was produced, and a regulus like disulphide of copper, which contained "moss copper" in cavities near the surface. At the bottom of the crucible there was also some metallic copper, through which disulphide of copper was diffused.

Disulphide of copper exposed to the action of hydrogen at high temperatures.—According to Berthier[9] and H. Rose[1] disulphide of copper is not changed when heated to redness in a stream of hydrogen. The following experiments were made by A. Dick in my laboratory. Perfectly dry hydrogen was passed over disulphide of copper in a tube of German glass heated until the glass softened. Sulphuretted hydrogen was evolved in small quantity; and the residue, where it had been exposed to the greatest heat, had a coppery aspect.

Disulphide of copper exposed to the vapour of water at a high temperature.—Disulphide of copper was prepared by heating together electrotype copper and sulphur. The product was reduced to powder and again heated with sulphur in order that no metallic copper might remain. A porcelain tube, coated externally with a mixture of fire-clay and asbestos, was fixed in a furnace capable of producing a white heat. The disulphide in powder was placed in a little porcelain boat, to the bottom of which asbestos was attached by platinum wire so as to prevent its sticking to the tube. Steam was passed through the tube, and the boat gradually pushed into the hottest part. At first sulphuretted hydrogen was evolved, as detected by its smell, and free sulphur was deposited in the condensed steam. The odour of sulphurous acid in admixture with sulphuretted hydrogen was also clearly detected by Dick and myself, notwithstanding these gases mutually decompose each other, with the formation of water and the separation of sulphur. After a short time these gases ceased to escape with the steam, or, if they did, it was only in very small quantity. During three-quarters of an hour the tube was heated nearly to whiteness, and a good current of steam was kept up all the time. The boat was then gradually withdrawn

[9] Tr. des Essais, 2, p. 402.

[1] Jahres-Bericht. Berzelius, 1827, p. 110.

from the tube by means of a wire, and, when the temperature was reduced to about 100° C., it was taken out of the steam. The product consisted of several globules of melted disulphide, the surfaces of which were covered with little excrescences of metallic copper. In a second experiment a considerable quantity of globules of copper were obtained. The experiment was repeated a third time with the same results.

In 1837 Regnault experimented on this subject. He found that, at a red heat, the vapour of water only exerts a very feeble action upon disulphide of copper, metallic copper and sulphuretted hydrogen being separated in small quantity. At a strong white heat, however, the disulphide is energetically decomposed, hydrogen being copiously evolved along with sulphuretted hydrogen, and drops of sulphur being condensed in the tube. After seven hours the disengagement of gas ceased, when it was ascertained that the disulphide of copper had been completely reduced to the metallic state. The button of copper was very brilliant. Regnault explains the production of free hydrogen by the decomposition which sulphuretted hydrogen undergoes at a high temperature. He found that when this gas is exposed *per se* to a white heat, it is only very partially decomposed; and, as the presence of the vapour of water cannot favour the decomposition, he supposes that, in the foregoing experiment, the copious evolution of hydrogen may be due to the fact that sulphuretted hydrogen in the nascent state is much more easily decomposed than when it has acquired the gaseous state.[2] In reference to these results Gmelin inquires what becomes of the water?[3] This question may be readily answered. If the hydrogen of the water combine with sulphur, its oxygen must combine with copper to form oxide of copper; but the oxide of copper thus formed would, at the high temperature of the experiment, immediately act upon the unchanged disulphide with which it may be in contact, forming sulphurous acid and metallic copper. Part of the sulphurous acid may escape from the tube, as was the case in Dick's experiment, while the remainder may be decomposed by the sulphuretted hydrogen, with the formation of water and free sulphur.

Metallic copper exposed to the action of the vapour of water at high temperatures.—According to Regnault, when the vapour of water is passed over metallic copper in a porcelain tube heated nearly to whiteness, hydrogen gas is evolved in very sensible quantity. On continuing the operation during three or four hours, from 80 to 90 cubic centimetres of inflammable gas were collected. After the conclusion of the experiment the tube was broken, when the anterior part was found to be coated with a very thin layer of black matter which dissolved in acids and presented the characters of oxide of copper. Regnault supposes that this layer of oxide may have been formed by the volatilization of a little copper and its oxidation in that very finely divided state by the vapour of water. The copper in the tube was melted, and had a fine metallic lustre; at some points of its surface it presented an

[2] Ann. des Mines, 3. s. 11, p. 44.
[3] Handbook of Chem. Cavend. Soc. 5, p. 421.

excessively thin and deeper coloured film of oxide. This experiment proves that metallic copper is only capable of decomposing the vapour of water at a very high temperature, and then only so feebly that it would be impossible to produce complete oxidation. It might be objected, as Regnault remarks, that copper only decomposed the vapour of water under the influence of the silica of the tube. In order to ascertain the force of this objection he exposed a mixture of copper turnings and finely divided silica (as obtained by the action of water on hydrofluosilicic acid) to the action of the vapour of water in a porcelain tube heated to whiteness. The operation was continued during four hours, but hydrogen was not disengaged in greater quantity than in the first experiment. The metal was only melted in drops amongst the silica in certain places; in others it had preserved its form; its surface was not more brilliant than before the experiment; its colour had become very rosy, like that of copper containing oxygen. No trace of silicate of either of the oxides of copper could be detected.[4]

Disulphide of copper heated with carbon.—According to Berthier carbon slowly reduces disulphide, but only at a very high temperature.[5] The following experiment was made by R. Smith :—200 grains of disulphide were exposed to a high temperature in a brasqued crucible; the product consisted of 189·5 grains of unchanged disulphide and 8·5 of metallic copper. Sulphur must be evolved in combination with carbon.

Disulphide of copper heated with iron.—The experiments were made by W. Baker.

1. Cu^2S = 1000 grains.
   Fe (in filings) = 353 do.

The mixture was exposed during twenty minutes to a strong red heat in a crucible with a luted cover. The product was melted, and consisted of regulus, and a button of metal weighing 538 grains. The metal was analysed by Mr. Tween, and found to have the following composition :—

Copper	62·45
Iron.....	31·70
Sulphur	3·85
	98·00

2. Cu^2S = 1000 grains.
   Fe^2 = 700 do.

The product was melted, and consisted of regulus and metal; it was brittle and slightly crystalline on the lower and external parts; its fractured surface was uneven, and had a dark iron-grey colour with a reddish tinge.

3. Cu^2S = 1000 grains.
   $Fe^2\frac{1}{2}$ = 910 do.

The mixture was exposed in a crucible with a luted cover during forty-five minutes to the high temperature of a furnace heated with

[4] Ann. des Mines, 3. s. 11, p. 26.

[5] Tr. des Essais, 2, p. 402.

anthracite. There was no separation into regulus and metal. The product was brittle and purple coloured; its fractured surface was uneven, crystalline, especially the lower portion, and reddish dark grey.

4. Cu^2S = 1000 grains.
   Fe^4 = 1410 do.

The product was melted and dark reddish grey. There was no distinct separation into regulus and metal. On its upper surface was a thin layer of compact, non-crystalline, dark grey regulus, below which the mass was crystalline. It contained moss-copper, especially in the centre, and at the depth of about one-third from the top, where there appeared to have been a cavity. Mixed with the moss-copper I observed distinct dark grey crystals, resembling those of disulphide of copper, which are sometimes produced during the process of copper-smelting.

From the preceding experiments it appears that disulphide of copper is only partially reduced to the metallic state when heated with iron. A double sulphide of copper and iron is formed; upon which iron exerts no reducing effect.

Disulphide of copper heated with zinc.—The experiments were made by R. Smith.

1. Cu^2S = 320 grains.
   Zn (in fine powder) = 128 do.

An intimate mixture was made and exposed to a bright red heat during twenty minutes in a Cornish crucible with a luted cover. The product weighed 246 grains, the loss in weight being 202 grains; it consisted of a thin layer of a dark bluish-grey regulus, and a button of metal of the colour of brass; they adhered together tenaciously. The regulus contained 58·4 per cent. of copper, and the button 81·8 per cent.

2. Cu^2S = 160 grains.
   Zn^2 = 128 do.

The product weighed 182 grains, the loss in weight being 106 grains. It consisted of a layer of regulus weighing 119 grains, and a button of metal weighing 63 grains. The regulus was compact, brittle, finely granular on fracture, and crystalline on the exterior; its upper surface was partially covered with moss-copper; it contained 62·37 per cent. of copper. The button was well melted, of the colour of brass, and contained 80·9 per cent. of copper. The loss of copper amounts to 2·82 grains. About two-sevenths of the copper of the disulphide were reduced to the metallic state.

Disulphide of copper heated with lead.—The experiments were made by R. Smith. The lead was prepared by constantly shaking it during solidification after fusion, and finely sifting the powder thus obtained. The materials were intimately mixed and heated in Cornish crucibles, covered, but not luted.

1. Cu^2S = 400 grains
   Pb (in fine powder) = 520 do.

The product was melted, and consisted of regulus, and a button of

metal weighing 495 grains. They adhered tenaciously to each other. The regulus was compact, hard, purplish-grey, and semi-vitreous in lustre. The metal resembled lead, was malleable, but could be easily broken in two; it contained 10·3 per cent. of copper.

2. $2Cu^2S$ = 400 grains.
   Pb^3 = 780 do.

The description of the product of the last experiment applies equally to that obtained in this. The button of metal weighed 753 grains, and contained 8·84 per cent. of copper.

3. Cu^2S = 400 grains.
   Pb^2 = 1040 do.

The product was similar in characters to that of the first experiment. The button of metal weighed 1019 grains, and contained 6·76 per cent. of copper.

In the three preceding experiments, the total amounts of copper reduced to the metallic state were respectively as follow: 50·99, 66·57, and 68·88 grains; the amount of copper in the disulphide employed being the same in each experiment, namely, 320 grains. Hence it may be concluded that when disulphide of copper is heated, either with a small or a large quantity of lead, between one-fifth and one-sixth of the copper is reduced to the metallic state.

Disulphide of copper heated with tin.—Experiment by Mr. W. Baker in the metallurgical laboratory.

Cu^2S = 1000 grains.
Sn (in powder) = 741·7 do.

An intimate mixture was made and heated to bright redness during ten minutes in a Cornish crucible, enclosed in another crucible with a luted cover. The inner crucible with its contents was weighed before and after the experiment: the loss of weight amounted only to 18 grains.

The product consisted of regulus, and a button of metal, which were easily separated from each other. The regulus which contained tin was compact, crystalline, and more grey than disulphide of copper. The metal was crystalline, with a largely lamellar fracture, very brittle, and white. It had the following composition:—

Tin	65·17
Copper	33·25
Sulphur	0·37
	98·79

It may, therefor, be regarded as a definite alloy of the formula CuSn. The reaction which occurs may be expressed by the following equation:—

$$2Cu^2S + Sn^2 = CuSn + (Cu^2S + Cu, Sn, S.)$$

Thus in two equivalents of disulphide of copper, one equivalent of copper is replaced by one of tin; and the equivalent of copper so replaced forms a definite alloy with one equivalent of tin. The regulus

may be considered as resulting from the substitution of one equivalent of tin for one of copper in two equivalents of the disulphide.

Disulphide of copper heated with antimony.—The experiments were made by R. Smith.

1. Cu^2S = 160 grains.
   Sb = 258 do.[6]

An intimate mixture was made. The product weighed 409 grains, the loss being 9 grains; it consisted of regulus and a button of metal, which adhered tenaciously together. The regulus amounted to about one-fourth of the bulk of the whole mass; it was compact, fine-grained, and purplish grey; it contained 57·48 per cent. of copper. The button of metal resembled antimony, and had a largely lamellar fracture; it contained 19·2 per cent. of copper.

2. $3Cu^2S$ = 240 grains.
   Sb = 129 do.

The product weighed 365 grains, the loss being 4 grains; it consisted of regulus and metal similar in appearance to those of the last experiment. The regulus and metal adhered so firmly together that it was impossible to separate them so as to obtain the weight of each with any degree of accuracy. The regulus contained 57·9 per cent. of copper. The metal had the following composition:—

Copper	33·40
Antimony (by loss)	60·56
Sulphur	6·04
	100·00

Copper heated with tersulphide of antimony.—The experiments were made in the metallurgical laboratory by my former pupil, Mr. Ambrose Tween. The old atomic weight of antimony, 129, was taken.

1. Cu^3 = 190 grains.
   SbS^3 = 354 do.

The copper was employed in the state of wire cut into small pieces. An intimate mixture was made, and exposed during twenty minutes to a bright red heat, in a Cornish crucible with a luted cover.

The product weighed 517 grains, the loss being 27 grains; it consisted of regulus and a button of metal, which adhered very tenaciously together. The regulus and metal were composed as follows:—

	Regulus.	Metal.
Copper	47·53	3·86
Antimony (by loss)	29·32	95·97
Sulphur	23·15	0·17
	100·00	100·00

By adopting the recent atomic weight of 120·3, as established by

[6] The old equivalent of 129 was taken.

Schneider and H. Rose, the composition of the regulus may be nearly expressed by the formula

$$3Cu^2S + SbS^3$$

2. Cu^6 = 380 grains.
   SbS^3 = 354 do.

The product weighed 689 grains, the loss being 45 grains; it consisted of regulus and metal, which adhered firmly together. The regulus and button of metal were composed as follows:—

	Regulus.	Metal.
Copper	66·44	42·54
Antimony (by loss)	16·91	57·06
Sulphur	16·65	0·40
	100·00	100·00

3. Cu^{12} = 761 grains.
   SbS^3 = 354 do.

The product weighed 1087 grains, the loss being 28 grains; it consisted of regulus and metal, which could not be separated, and were composed as follows:—

	Regulus.	Metal.
Copper	75·9	66·72
Antimony (by loss)	22·8	32·98
Sulphur	1·3	0·30
	100·0	100·00

4. Cu^{18} = 1141 grains.
   SbS^3 = 354 do.

The product weighed 1474 grains, the loss being 21 grains; it consisted of regulus and metal, which adhered firmly together, and were composed as follows:—

	Regulus.	Metal.
Copper	77·36	75·90
Antimony (by loss)	21·31	24·03
Sulphur	1·33	0·07
	100·00	100·00

Disulphide of copper heated with protoxide of lead.—The experiments were made by W. Baker, and the quantitative determinations by A. Tween. The materials were intimately mixed, and heated in covered Cornish crucibles during about ten minutes, at a temperature just sufficient to effect perfect fusion.

1. Disulphide of copper = 400 grains.
   Litharge = 2000 do.

The product consisted of slag, regulus, and a button of metal; the button weighed 410 grains, and resembled lead; it contained 22·55 grains of copper, or 5·5 per cent. The slag appeared to be composed of protoxide of lead and dioxide of copper.

2. Disulphide of copper = 100 grains.
   Litharge = 2000 do.

The product consisted of a crystalline, opaque, reddish-brown slag, and a button of metal weighing 394 grains; it resembled lead, and contained 22·85 grains of copper, or 5·8 per cent.

3. Disulphide of copper	=	100 grains.
Litharge	=	2500 do.

The product consisted of a slag like that of the last experiment, and a button of metal weighing 422 grains: it resembled lead, and contained 21·67 grains of copper, or 5·16 per cent.

Hence it appears that when disulphide of copper is heated with twenty times its weight of protoxide of lead, the whole of its sulphur is oxidized; for otherwise some regulus would have been obtained in the second experiment. The sulphur is converted into sulphurous acid, which, on escaping, causes the effervescence observed. About four parts by weight of protoxide of lead contain oxygen sufficient to convert the sulphur of one part of disulphide of copper into sulphurous acid, and the copper into dioxide; but, practically, a much larger quantity of protoxide of lead is required to produce this effect. The results of the preceding experiments tend to confirm the statement of Berthier, that, when litharge is combined with a certain proportion of dioxide of copper, it ceases to exert any action upon disulphide of copper, although each oxide separately has the power of decomposing this sulphide.

Disulphide of copper heated with sulphate of lead.—According to Berthier, sulphate of lead attacks simultaneously both elements of the disulphide; so that neither copper, nor an alloy of copper and lead, ever results from the reaction between these two substances. The product consists of a regulus, which appears to contain sulphide of lead, and a red slag composed of oxide of lead and dioxide of copper, sulphurous acid being evolved. In order to decompose the whole of the disulphide of copper, it would be necessary to mix it with at least seven times its weight of sulphate of lead; and the product resulting from such a mixture would be a slag formed of oxide of lead and dioxide of copper.[7]

Disulphide of copper heated with nitre.—The action is energetic at a nascent red heat. When the quantity of nitre is sufficient to convert the whole of the sulphur into sulphuric acid, and access of air is prevented, the whole of the copper is reduced, and the slag consists entirely of sulphate of potash. In order to moderate the deflagration, it is necessary to add to the mixture a considerable quantity of alkaline carbonate (Berthier). The following equation should express the reaction:—

$$Cu^2S + KO, NO^5 = Cu^2 + KO, SO^3 + NO^2.$$

When the nitre is in excess, the slag will contain dioxide of copper.

Disulphide of copper heated with caustic soda.—According to Berthier, the disulphide is partially decomposed, with the separation of metallic copper, and the formation of sulphate of soda, and a double sulphide of sodium and copper. The presence of charcoal much promotes the

[7] Tr. des Essais, 2, p. 406.

desulphurization. From a mixture of 1 part of disulphide and 2 parts of caustic soda, Berthier obtained 0·32 of copper; and from a mixture of 1 part of disulphide, 1 of caustic soda, and 0·4 of charcoal, he obtained 0·54 of copper. The first amount is nearly the same as that we obtained by heating a mixture of disulphide, carbonate of soda, and charcoal.

The following formula expresses the reaction:—

$$4Cu^2S + xCu^2S + 4NaO = NaO,SO^3 + 3NaS, xCu^2S. + Cu^8.$$

Disulphide of copper heated with carbonate of soda.—The experiments were made by R. Smith.

1. A mixture of 200 grains of disulphide of copper, and a considerable quantity of carbonate of soda, was heated in a covered Cornish crucible. No metallic copper was separated. The product consisted of a brownish black slag, and a button of regulus like disulphide of copper. The experiment was repeated with precisely the same result.

2. A mixture consisting of 200 grains of disulphide of copper, about 400 of dry carbonate of soda, and 50 of charcoal, was heated in a covered Cornish crucible. The product consisted of a somewhat crystalline black slag, and a brittle metallic button resembling copper, and weighing 61 grains. The experiment was repeated with the same quantities, and a button of metal was obtained weighing 64 grains. Taking the mean of the weights of copper obtained in both experiments, the amount of copper reduced is somewhat more than 39 per cent. of the total copper.

Berthier states that when a mixture of disulphide of copper and carbonate of soda in the ratio of $Cu^2S : 3NaO,CO^2$ is exposed to a high temperature in a brasqued crucible, the reduction of the copper is nearly complete. According to the same authority, elevation of temperature singularly favours the reaction.

According to Berthier, disulphide of copper is partially reduced when heated with the pearlash of commerce; because the latter always contains some caustic potash: with 6 parts of pearlash to 1 of disulphide, only 0·4 of copper is obtained, and no more is separated by increasing the proportion of flux.

Disulphide of copper heated with baryta or lime.—Baryta and caustic lime partially decompose disulphide of copper like the alkalies, at least in the presence of carbon; but the copper separated remains diffused in the form of shots through the double sulphide of copper and barium, or calcium, which is formed and does not thoroughly melt even at a very high temperature, on account of admixture with a certain amount of baryta or lime (Berthier).

Disulphide of copper heated with cyanide of potassium.—The experiments were made by R. Smith. The mixtures were heated in covered Cornish crucibles. The disulphide is partially reduced.

	1. Grains.	2. Grains.	3. Grains.	4. Grains.	5. Grains.
Disulphide of copper	100	100	100	50	50
Cyanide of potassium	400	800	1000	550	300
Charcoal	20	40	50	50	..
Copper reduced	46	43	41	23	20
Do. do. on repeating the experiment	..	..	..	21	21

Observations.—1. The copper was very fine and tough. 2 and 3. The slag was black. 4. The mixture was covered with common salt. 5. Plumbago crucibles were employed.

Copper and dioxide of copper.—Copper in the state of fusion has the property of dissolving dioxide of copper to a considerable extent. When it contains this oxide to the maximum, it is technically termed "*dry copper*" by English copper-smelters, or "*ueber-gaar*" by German smelters. Dry copper is distinguished by the following characters: it is brittle either when cold or hot, so that an ordinary ingot may be easily broken in two; the fractured surface is uneven, minutely granular, and without any appearance of fibre; it presents here and there the appearance of films of dioxide and globular cavities; it is dull, and of a comparatively deep purplish red colour; and, when cast in an open narrow mould of copper of the usual well-known form, the upper surface of the ingot is marked by a shallow longitudinal depression or furrow, extending nearly from end to end along the median line. Copper which contains much less than the maximum of dioxide is said to be more or less "dry;" and the degree of dryness is proportionate to the amount of this oxide present.

An ingot of copper in the *driest* state, which, through the kindness of the late Mr. Vivian, I saw laded from the furnace at the Hafod Works, has been examined by Dick in my laboratory, with a view to determine the proportion of dioxide contained in it.[8]

1. A portion of this ingot was rolled out as thin as possible, and the rolled metal was cut into small pieces, of which 132·34 grains were exposed to a current of dry hydrogen in a combustion tube heated to redness, and connected with a weighed tube containing chloride of calcium; the gas was previously passed through the tube in order completely to expel atmospheric air. When the temperature rose to redness, the gas which escaped had a distinct odour of sulphuretted hydrogen, and instantly blackened paper impregnated with a salt of lead. This result is remarkable, as showing that copper saturated with dioxide may yet retain a very sensible amount of sulphur. During the course of the experiment a slight metallic sublimate appeared in the cooler part of the tube, which, however, was much

[8] All the experiments by Mr. Dick on the metallurgy of copper, to be subsequently detailed, were made in the metallurgical laboratory, *expressly* for this work; and I not only consented to but urged their publication in extenso in the Philosophical Magazine for June, 1856.

too hot for the condensation of arsenic: it was found to contain lead, but its quantity was too small to admit of satisfactory examination. The chloride of calcium tube increased in weight 1·93 grain, which is equivalent to 10·21 per cent. of dioxide. In a second similar experiment upon another portion of the same dry copper, the increase was 1·82 grain, which is equivalent to 9·34 per cent. of dioxide. Sulphuretted hydrogen was again detected at the beginning of the experiment. Precautions were taken to make it certain that the hydrogen employed contained neither water nor sulphur. It is scarcely to be expected that this method would yield uniform and exact results, unless the copper were in a very much finer state of division than that operated upon.

2. An attempt was made to deduce the oxygen of the dioxide from the loss occasioned by melting the copper in hydrogen. The apparatus employed for the purpose was a small Stourbridge clay crucible fitted with a perforated cover. It was filled with hydrogen by means of a small porcelain tube passing through the hole in the cover, and was heated by charcoal to the melting-point of copper. Great spirting occurred, and it was not possible to collect all the projected globules of copper, which adhered to the inner surface of the cover and sides of the crucible; so that the loss of weight, due to the reducing action of the hydrogen, could not be ascertained. Spirting took place even when the crucible was very gradually heated.

3. A weighed quantity of the dry copper was dissolved in nitric acid, and the solution was saturated with caustic potass, and boiled. The precipitate was collected on a filter, washed, ignited, and weighed: it was then evaporated with nitric acid, and exposed to a red heat until its weight became constant. From the protoxide of copper thus obtained, the proportion of copper which it should have contained, supposing it to have been pure, was calculated; and the difference between the weight deduced and that of the original copper was estimated as oxygen. As commercial copper is never perfectly free from certain other metals, and probably also other matters, this method cannot yield absolutely exact results; yet, as the proportion of these foreign matters is comparatively very small, the error cannot be very great. In one experiment, 10·73 grains of dry copper gave 13·18 of protoxide, which is equivalent to 98·09 per cent. of copper; and in another, 9·17 grains gave 12·26 of protoxide, which is equivalent to 98·01 per cent. of copper. The difference estimated as oxygen corresponds, in the first experiment, to 17·04 per cent. of dioxide of copper; and, in the second, to 17·74 per cent.

Karsten found that copper which was purposely made *very dry*, and could not be forged at any temperature without crumbling to pieces, contained 13·47 per cent. of dioxide, and had only a specific gravity of 8·0552; whereas it had previously, while in the state of maximum malleability, a specific gravity of 8·7574.

According to Karsten, the effect of the presence of dioxide of copper in copper is to diminish the tenacity of the metal less at high than at ordinary temperatures; and when *pure* copper contains 1·1 per cent.

of dioxide, it is no longer sufficiently malleable to admit of being worked at ordinary temperatures without splitting into laminæ and cracking at the edges. When the proportion of dioxide amounts to 1½ per cent. the decrease in tenacity is very perceptible at high temperatures, and the copper is brittle whether cold or hot, or, in technical language, it is both "*cold-short*" and "*red-short*."

When copper which is smelted on the large scale is in the highest degree malleable at all temperatures, it is technically said to be "at tough pitch" by English smelters, or "hammer-gaar" by German smelters. In this state it is usually cast into flat rectangular cakes called "tough cake," a form suitable for rolling or hammering. No commercial copper is pure, but in the preparation of tough cake a notable quantity of lead is always expressly mixed with the copper just before it is laded from the furnace into ingot moulds. The reason of this addition of lead will be stated hereafter. When copper at tough pitch is cast into a narrow open ingot mould, the upper surface of the ingot is flat, presenting neither furrow nor ridge. When such an ingot is broken in two cold, its fractured surface is even, close-grained, free from fibres or cavities, presenting, especially towards the centre, numerous shining grains of a bright metallic lustre; its colour is fine salmon-red, neither purplish-red nor orange. It is very interesting to watch the successive changes in external characters which copper undergoes in its passage from *dry* copper to *tough pitch* by the gradual, though not complete, reduction of the dioxide of copper. As the reduction proceeds, the fractured surface of the ingot becomes more and more even and acquires a paler and purer red colour, while the furrow on the upper surface becomes less and less distinct until it at last disappears altogether. When an ounce or so of tough-pitch copper is laded from the furnace and, after it has become cold, broken in two, its fractured surface is pale red and very finely fibrous, and has a characteristic silky lustre. The fracture may be conveniently obtained by nicking the piece of copper with a chisel, fastening it in a vice on one side of the nick, and bending the other with pliers backwards and forwards until it breaks. The toughness of the copper is proportionate to the number of times which it may thus be bent without breaking.

An ingot of tough-pitch copper which was laded from the furnace at the Hafod Works in my presence has, together with other specimens of commercial copper in this state, been examined by Mr. Dick in my laboratory with the following results:—1. Some of the metal was heated to redness in a current of dry hydrogen, when water was produced. Various experiments were made by this method with a view to determine the proportion of dioxide, just as in the case of dry copper, and the results obtained were equally discordant and unsatisfactory. The highest amount of dioxide indicated was 2·95 per cent. Towards the beginning of each experiment a trace of sulphuretted hydrogen was evolved, and, on testing the copper operated on, the presence of sulphur was detected. A slight metallic sublimate containing lead was formed, just as in the similar experiments upon *dry*

copper previously recorded. *Tough-pitch copper* which had thus been exposed in the state of wire or foil to the action of dry hydrogen at a red heat was found to have become *extremely brittle*, so that it could not be bent even once without breaking, and it had, moreover, lost the lustre of its surface. Flexibility could not be restored to the wire or foil by annealing at a red heat in a current of steam, which was employed because it exerts neither an oxidizing nor a reducing action. The same loss of flexibility occurred when hydrogen was replaced by carbonic oxide or coal-gas. The brittleness thus induced seems to be due to the porosity occasioned by reduction of the dioxide of copper diffused through the copper, and must be distinguished from the brittleness which the copper acquires by being *melted* in any of these reducing gases. If *tough-pitch* copper so melted be rolled out into foil—which may be done, though the metal cracks somewhat at the edges—and afterwards heated to redness in any of these gases, it will not become in the least degree brittle. Malleable electro-deposited copper, which it was certain contained no dioxide, either before or after fusion under charcoal, acquired not the slightest brittleness by exposure to the action of those gases at a red heat. These results have an important practical bearing, and are worthy of particular attention.

2. An attempt was made to deduce the amount of dioxide of copper in commercial copper-wire—which is always made from tough-pitch copper—from the loss occasioned by melting in hydrogen. Spirting took place, and though in a less degree than in former experiments of the same nature, yet sufficiently to render the method inaccurate.

3. A known weight of copper-wire was melted under charcoal—purified, as in all these experiments—with a view to deduce the amount of dioxide from the loss consequent on its reduction. Even when heat was very slowly applied the same kind of spirting sometimes took place, so that after each experiment the charcoal in the crucible was always washed by decantation to separate and collect any globules of copper which might have been projected into it. It will be shown hereafter that when copper is melted under charcoal, it certainly does not take up more than a very minute quantity of, if any, carbon.

Two different samples of copper wire, A and B, were subjected to experiment. A was thicker than B.

A. 218·24 grains lost by melting under charcoal 0·76 grain, which, estimated as oxygen in combination with copper, is equivalent to 3·10 per cent. of dioxide.

B. 176·48 grains lost by similar treatment 0·635 grain, which is equivalent to 3·37 per cent. of dioxide.

A contained 0·17 per cent. of lead, but no antimony could be detected in it. Its specific gravity was 8·853. B contained 0·29 per cent. of lead and 0·31 per cent. of antimony. Its specific gravity was 8·733. In a sample of commercial sheet-copper 0·27 per cent. of lead was found, but no antimony. Not one of these varieties of copper, after fusion under charcoal, could be hammered out at a *dull red heat* without cracking at the edges, although each could be hammered out

cold without cracking in the least degree. The pieces employed to test malleability weighed from 150 to 200 grains each. Similar pieces cut from the tough-pitch ingot which I obtained at the Hafod Works could not, after fusion under charcoal, even be hammered out cold without cracking at the edges. The amount of lead in this copper was not ascertained. Russian copper coin, which is said to be esteemed on account of the purity of the metal, was found to contain oxygen, and yet, after fusion under charcoal, it could be hammered out, even at a red heat, without cracking much. This seems to indicate a considerable degree of purity, though inferior to that of the electrotype copper employed in these experiments.

Several experiments were made with the view of finding some means of remelting *tough-pitch* copper in crucibles without causing any variation in the amount of dioxide contained in it. Commercial copper wire was plunged under common salt in a state of fusion and melted, but the copper could not afterwards be hammered out at a dull red heat without cracking, though electrotype copper which had been treated in the same way could be hammered out either cold or at a dull red heat without in the least cracking. Similar results were obtained when chloride of calcium was substituted for common salt. Copper suffers a sensible loss of weight by fusion under these salts. Thus, in one experiment, the wire B lost by fusion under common salt 2·44 per cent. in weight; in a second experiment 2·05 per cent.; and in a third, at a temperature just sufficient to melt copper, 1·35 per cent. The loss of weight was much greater when chloride of calcium was employed, amounting in one instance to not less than 7·17 per cent. No similar experiments were made with electrotype copper. When the common salt in which the metal had been melted was dissolved in water, insoluble matter was left, which contained both copper and chlorine. This deserves investigation. It may, possibly, be a compound of dioxide and dichloride of copper.

When tough-pitch copper is kept melted under charcoal during a sufficient time and is then laded into a narrow open mould, the upper surface of the ingot when cold presents a distinct ridge along the median line. This ridge is sometimes of considerable height. In the act of solidification globules (Streu or Sprütz-kupfer of the Germans) of melted copper may be projected with force along the line on which the ridge will be formed. The copper is more or less brittle, so that the ingot may be easily broken in two. Its fractured surface is more uneven than that of tough-pitch copper, and appears fibrous throughout; it frequently presents small, irregular, tube-like cavities, of which the direction is from the sides and bottom of the ingot towards the median line along the upper surface, and through which gas appears to have escaped; its colour is paler and less red than the fractured surface of tough-pitch, and strongly inclines to orange. The appearance of the surface of the ingot suggests the notion that, after the upper surface had solidified in a certain degree, the still liquid, but more or less viscous, copper within had been squeezed through the upper surface along the line of least resistance. Copper in this state

is said by English copper-smelters to be "*overpoled*"—the reason of which appellation will be given hereafter—and by the German smelters it is called "*zu junges Kupfer*." The cause or causes of this remarkable change in the external characters of copper will be presently considered.

Copper and carbon.—According to Karsten,[9] when pure copper is imbedded in lamp-black and exposed first to a strong red heat during several hours, and afterwards to the melting-point of copper, it may combine with as much as, but not more than, 0·2 per cent. of carbon. Copper containing this maximum proportion of carbon is distinguished by its pale yellowish-red colour and very strong metallic lustre, and at a low red heat it crumbles under the hammer. When the proportion of carbon does not even exceed 0·05 per cent. copper cannot be forged or rolled at a high temperature without splitting into laminæ and readily cracking at the edges. On the contrary, the presence of carbon scarcely affects the tenacity of copper at ordinary temperatures. The rigidity and brittleness which copper containing carbon acquires when hammered out cannot be removed by annealing at low temperatures, and, on this account, such copper is unsuited to fine plated work on the old system of plating copper with gold or silver. Such are the characters which Karsten ascribes to copper containing carbon.

As this subject is one of much importance in the metallurgy of copper, the evidence in support of the existence of a combination of copper and carbon must be examined with care. Karsten properly remarks that it is very difficult to determine with certainty the highest amount of carbon which may be taken up by copper. He adopted the following method of analysis. The copper was left in an aqueous solution of nitrate of silver, when the carbon—supposing it to be the only foreign matter present—was left undissolved in admixture with the precipitated metallic silver while the copper was completely dissolved in the state of nitrate. A button of copper weighing from 8 to 10 grammes was found to be wholly converted into nitrate of copper by being left in an aqueous solution of nitrate of silver during 6 or 8 days. The precipitated silver is dissolved by dilute nitric acid, and the quantity of the insoluble residue of carbon is so small that it only becomes visible after diluting the solution of nitrate of silver considerably and then gently warming it. Karsten anticipated the obvious objection which may be made to this process, namely, that the carbon, especially in this finely divided state, would probably be acted upon in a greater or less degree by the nitric acid employed to dissolve the precipitated silver. Moreover, Karsten presents us with no evidence to prove that any dark-coloured residue which may have been observed after dissolving the silver by nitric acid was carbon, either wholly or in part.[9]

It has long been known, that when *commercial copper*, even of the purest kind, is kept melted in contact with carbonaceous matter, so as

[9] Sys. der Metall. V. p. 231 et seq., 1832.

completely to prevent the action of the oxygen of the atmosphere, it acquires the properties which Karsten ascribes to copper supposed to contain carbon. Some years ago a specimen of "best selected" copper, which I knew had been prepared with particular care by Messrs. Newton, Keates, and Co., was subjected by myself to the following treatment:—It was reduced to powder by pounding it while hot in a mortar. The finest of this powder, as obtained by sifting, was mixed with a large quantity of powdered wood-charcoal, and heated in a covered crucible during many hours, at about the temperature of melted copper. When cold the crucible was opened. The copper was melted into small round shots, which were diffused through the charcoal. By blowing with bellows the charcoal was removed. The residual copper was re-melted in a crucible under charcoal powder, and cast, by an experienced caster of Birmingham, into a flat ingot in a closed iron mould, which had been duly coated with oil and charcoal, and then gently heated. The ingot was carefully rolled at Mr. Clifford's mill in the same town, without cracking at the edges; and a piece of the rolled metal was drawn out into wire; and yet I had many times tried in vain to roll ingots of the same kind of copper, which had not been previously heated in the manner described with charcoal powder. Although the copper could be rolled, yet it could not be forged at a red heat without crumbling to pieces. The metal was melted under varying conditions of temperature under charcoal, as well as with the surface exposed to the air; and yet in no instance could it afterwards be rolled without cracking at the edges, notwithstanding the rolling was conducted with great care and under different conditions of temperature. A piece of the sheet obtained from the copper heated with charcoal was placed on platinum foil and immersed horizontally in a solution of sulphate of copper: in the same solution, at some distance above, and parallel to, the foil, was fixed a plate of copper, which was connected with the negative pole of a constant battery, the platinum foil being connected with the positive pole. The whole was thus left until everything capable of being removed by the voltaic current from the sheet of copper on the platinum foil had been transferred to the plate of copper above. A very small quantity of dark-coloured matter was left on the platinum, in which any carbon which might have existed in the copper ought to have been present; but I did not succeed in satisfying myself of the presence of carbon, which, however, I am sure, could only have formed a small proportion of the residue in question.

Some years afterwards, Mr. Dick, at my request, investigated in the metallurgical laboratory this, amongst other subjects relating to the metallurgy of copper. The copper in which carbon was sought in the foregoing experiment was submitted to very careful examination, and was found to contain a notable quantity of silicon, and a small quantity of phosphorus and iron. Now it will be shown that when copper is exposed to a long-continued high temperature in contact with carbon in admixture with silica or phosphate of lime, it will take up silicon or phosphorus; and it will be further shown that when

"best selected" copper contains only a very minute proportion of various foreign matters—amongst which may be mentioned silicon and phosphorus—it may be re-melted in a crucible, and cast into ingots capable of being rolled without cracking at the edges. Hence it may be inferred that the silicon and phosphorus in the copper in question were derived, at least chiefly, from the ashes of the charcoal with which it was heated, and in sufficient proportion to affect in a striking degree the working qualities of the metal.

In the following experiments Mr. Dick employed electrotype copper, which was prepared from sulphate of copper at Messrs. Elkington and Co.'s Electro-plate Works in Birmingham; and although not necessarily pure, yet it is likely to be free from lead, and some other foreign matters, which may occur in smelted commercial copper. The charcoal powder was digested in hydrochloric acid, and afterwards thoroughly washed with water.

1. Electrotype copper, melted in small pieces under charcoal, could be hammered out without cracking, whether cold or hot.

2. Some rather larger pieces of electrotype copper were imbedded in charcoal powder and heated for about half an hour at a temperature approaching whiteness. The contents of the crucible were then stirred with a piece of wood, so as to cause the metal to sink to the bottom; after which it was cast into an ingot mould.

3. Several pieces of electrotype copper were placed in a brasqued crucible, which was then completely filled with charcoal powder, covered, and exposed to a temperature approaching whiteness for about an hour. The crucible was left to cool gradually in the furnace. The copper thus treated was re-melted under similar conditions and sent to Birmingham, together with that obtained in the last experiment, to be rolled into sheet and drawn into wire, with the direction that they might be treated exactly like ordinary copper when subjected to these processes. No mention was made of the treatment which the copper had received. They rolled well into thin sheet, and were drawn into tolerably fine wire. The report received from the rollers was that, although the casting was not good, the metal was fit for any work.

4. A piece of the sheet obtained in the last experiment was boiled in a solution of caustic potass, to remove any oil which might be present; it was then washed and dried, when it weighed 221·10 grains. It was laid in a platinum basin, immersed in a solution of sulphate of copper. The basin was connected with the positive pole of a voltaic battery, and a plate of copper connected with the negative pole was fixed in the solution above the basin. The whole was protected from dust, and left until the residue from the copper in the basin was very small. It still contained a little metallic copper, which was dissolved out by a solution of sesquichloride of iron mixed with a little hydrochloric acid. The insoluble residue was then washed by decantation and dried, when it weighed 0·08 grain; its colour was very dark grey, nearly black. When a portion of it was heated on platinum foil, it evolved a slight and peculiar odour, glowed for an instant, and left a small amount of fixed matter,

Another portion, weighing 0·012 grain, was introduced on a very small piece of platinum foil into a small glass tube, of which one end dipped into baryta water protected from the air, while the other was connected with an apparatus from which a very feeble current of air, quite free from carbonic acid, could be sent. A current of air was passed over the platinum, and produced no cloudiness in the baryta water. That part of the tube containing the platinum foil was then heated by means of a spirit lamp, when a very slight deposit of the colour of sulphur appeared in the cold part of the tube; but when the platinum became red hot, every bubble of air, as it traversed the baryta water, caused a white precipitate, which dissolved with effervescence on the addition of excess of hydrochloric acid. The residue upon the platinum foil weighed 0·003 grain; it had a light reddish colour, and dissolved almost entirely in hydrochloric acid; the insoluble portion was, probably, a minute quantity of silica derived from silicon, which the copper may have extracted from the charcoal. The solution contained a trace of iron, but was not turned blue by ammonia; the quantity was too minute for any further experiments. The weak point in this evidence as to the presence of carbon is, that the precipitate in the baryta water might have been sulphite, and not carbonate, of baryta; and that sulphurous acid might, not to say must, have been formed, is evident from the sulphur which was evolved and condensed at the beginning of the experiment. The copper employed in the foregoing experiment was tested for sulphur, and found to contain 0·05 per cent. of that element.[1] We are, therefore, not justified in concluding that this copper certainly contained carbon. It is hardly probable that the sulphur was derived from the charcoal, which had been purified by washing, first with hydrochloric acid, and afterwards with water, or from the gases of the furnace; but it seems not improbable that the electrotype copper may have retained in pores some of the solution of sulphate of copper from which it was deposited: any sulphate so imprisoned would, in contact with copper at a high temperature, be reduced to disulphide.

5. Across the mouth of an ingot mould a copious flame of coal gas was maintained, and through the burning gas 336·9 grains of electrotype copper, melted under charcoal, were poured. The copper, which contracted sensibly in cooling, was rolled *without annealing*, during which it cracked a little at the edges. To free it from any adherent oil, it was boiled in a solution of caustic potash and washed; it was then acted on for a short time by dilute nitric acid, washed, digested in ammonia, washed well with dilute ammonia, and, lastly, with hot distilled water. In this state it was placed in a stoppered bottle filled with a filtered solution of sesquichloride of iron, which contained free hydrochloric acid and chloride of sodium. The bottle was digested in a water-bath during several days, and then allowed to stand at rest

[1] Other specimens may have contained less, or more, or none. The presence of this compound in electrotype copper was unfortunately not suspected till nearly the close of the investigation. The sulphur in this copper has been re-determined with the *greatest possible* care by Mr. Tookey, and found to amount only to 0·00259 (= Cu^2S 0·01279) in 100 parts of copper.

during one night. The clear supernatant solution was removed by a syphon to within a quarter of an inch from the bottom. The residual liquid was diluted and left at rest. Black matter subsided, which was thoroughly washed, and weighed after drying; the weight was 0·16 grain. A minute portion of this sediment was cautiously heated on platinum foil, when it glowed for an instant, yielding a black residue, which at a higher temperature melted. The whole of the remainder was mixed with a slight excess of litharge, which had been previously melted with free access of air, and put into a very small tube drawn out to a point and closed at one end, and connected at the other with a small weighed tube containing a few grains of fused hydrate of potash. Heat was then applied to the first tube, when there was instant partial reduction, with the separation of distinct globules of soft lead. The point of this tube was broken off, and a little drawn through the potash tube, just as in an ordinary organic analysis; the potash tube increased in weight 0·45 grain. It must be remembered that litharge is reduced when heated with disulphide of copper.

6. About 672 grains of filings of electrotype copper, which had been melted under charcoal, were mixed with freshly-ignited chromate of lead in a combustion tube connected with a Liebig's potash-apparatus. No gas was perceived to bubble through the potash solution. At the end of the process, some air having been drawn through the combustion tube, the potash apparatus was found to have increased 0·115 grain in weight. Assuming this to be carbonic acid, and that the whole of the carbon supposed to exist in the copper had been converted into carbonic acid, this increase in weight corresponds to 0·031 grain of carbon in 672 grains of copper, or only 0·0046 per cent.

The preceding data, it must be admitted, do not surely establish the fact that copper melted under, or exposed to a high temperature in contact with, charcoal, does combine with carbon; though they seem to indicate the probability that copper may under these conditions take up a very minute quantity. It may, however, be regarded as pretty certain that if copper have this power, it can only combine with a very minute proportion of carbon. But there is one point of practical importance which is proved by the foregoing experiments, namely, that *comparatively pure copper is not rendered brittle by being heated, or melted in contact with comparatively pure charcoal.* This conclusion will be further supported by the results of other experiments yet to be described. I much regret that the investigation, which had proceeded so far, should, from one cause or other, not have been resumed and carried to completion.

Overpoled copper.—As this variety of commercial copper—by which is meant such as is ordinarily produced in this country—is the result of the action of charcoal or other carbonaceous matter on copper containing dioxide while in a state of fusion, it is necessary to enquire whether the remarkable change which the metal undergoes during this process is due simply to the total reduction of the dioxide with which it was previously impregnated, or, as has been commonly

supposed, to the combination of carbon with the copper after total reduction of the dioxide; or, whether it may not depend on the joint operation of both these causes. One of the most characteristic properties of commercial overpoled copper is brittleness; but comparatively pure copper—such as the electrotype copper employed in the preceding experiments—may, after having been melted under charcoal, be hammered out hot or cold without cracking: it is also equally malleable after having been melted and cooled in hydrogen. Some of the copper thus treated was rolled out with smooth, or "wire" edges, to the thinnest foil. Here, then, is a wide distinction between overpoled commercial copper, and pure copper melted in contact with charcoal. Both kinds of copper may be perfectly deprived of dioxide, and both may equally be exposed in a melted state to the action of charcoal, and yet one shall be excessively brittle, and the other malleable at all temperatures. From these data the conclusion is inevitable, that the brittleness of overpoled commercial copper must depend upon the presence of some foreign matter. It cannot be due to the presence of carbon; for pure copper may be kept melted any length of time under pure charcoal without becoming brittle. Now, commercial copper is never perfectly free from certain other metals; and amongst those which very frequently occur may be mentioned lead and antimony. Although only a minute quantity of these metals may exist in copper, yet it may be quite sufficient to determine the brittleness of overpoled commercial copper. But tough-pitch commercial copper must equally contain these metals, and, nevertheless, it is malleable, hot as well as cold. However, in tough-pitch copper there is always present a certain proportion of dioxide of copper, which cannot be removed without brittleness resulting. The existence, therefore, of a certain proportion of dioxide of copper in commercial copper would seem to be essential to its malleability. This is precisely the conclusion at which Karsten had previously arrived. He states that while dioxide of copper, even in small proportion, decreases the malleability of *pure* copper while hot as well as cold, the presence of a certain amount of dioxide is essential in *impure* copper, in order that the brittleness of the metal at high temperatures may be as much as possible counteracted. He further remarks that the effect of all foreign matter in copper is specially to diminish its malleability in a greater degree at *high* than at low temperatures—in other words, to render it more "red-short" than "cold-short"—and that the dioxide diminishes the "red-shortness" of impure copper, so long as it does not exceed from $1\frac{3}{4}$ to 2 per cent.[2]

We have previously seen that tough-pitch copper in the form of wire or foil is rendered excessively brittle by exposure to the action of hydrogen or carbonic oxide at a red heat far below the melting-point of copper; and as there is no reason to suppose that these gases act in any other way than by reducing the dioxide contained in the copper, we may infer that the oxygen of the dioxide cannot be abstracted

[2] Sys. der Metall. 5, p. 248.

even from *solid* tough-pitch copper without destroying its malleability.

Admitting the preceding conclusion to be correct, it seems probable that the proportion of dioxide of copper required to produce the highest degree of malleability in tough-pitch copper will vary, to a certain extent, with the nature of the foreign metals, or other matters, which may be present in commercial copper. But this is a point which can only be determined by very careful experiments. It need scarcely be remarked that, as copper passes from the state of tough-pitch to that of overpoled to the maximum, the proportion of dioxide is gradually reduced, until at last not a trace remains; so that copper much overpoled, but not to the maximum, may yet retain a sensible amount of dioxide.

Concerning the mode of action of dioxide of copper we have not at present, so far as I am aware, any certain knowledge. Whether its action is simply mechanical, or whether the foreign metals present in commercial copper exist in all cases and in any degree as oxides in combination with dioxide of copper, future experiments must decide. It is well to repeat in this place that, although the proportion of dioxide in tough-pitch copper has been assumed to be equivalent to the oxygen actually found by experiment, yet, when other metals are present, it by no means follows that the whole of this oxygen is combined with copper to the exclusion of those metals. Indeed, an oxidized compound of copper, nickel, and antimony, called copper-mica, and having the formula $12(Cu,Ni)O+SbO^3$, is occasionally found in dry copper smelted from ores containing nickel and antimony.[3] In this formula it will be perceived that the copper is said to exist as protoxide, and not as dioxide.

It has been stated that when overpoled copper is laded under ordinary conditions into an open mould the surface of the ingot *rises*, and that in the case of a narrow ingot, it is thrown up so as to form a longitudinal ridge which is sometimes very distinct, and not less than a quarter of an inch in height. The cause of this has now to be considered.

1. When electrotype copper of the degree of purity used in the foregoing experiments was melted under charcoal in a crucible and left to cool therein, not only was there *no rising*, but, on the contrary, a considerable depression in the centre of the upper surface of the button. In a specimen in my collection which was prepared in this way by Mr. Dick is a cavity of considerable size near the centre of the upper surface of the button, and projecting into it are crystals of copper grouped branchwise, much like certain specimens of the native metal, or the so-called fern-leaves on the surface of the large round cakes of commercial antimony. The depression in the surface and the crystalline markings were uniformly observed in numerous repetitions of this experiment. It is manifest, therefore, that considerable contraction occurs in the centre of the mass during the solidification of the metal,

[3] Rammelsberg, Lehrb. der chem. Metallurgie, 1850, p. 210.

which acquires a very marked crystalline structure throughout. Another point of importance is, the fractured surface of electrotype copper which has been melted under charcoal and allowed to solidify in the crucible never presents any trace of vesicular structure.

2. When the same electrotype copper was melted under charcoal and poured into a mould in the usual way, without any precautions being taken, the surface of the ingot rose, and after cooling was either rough and tolerably flat or comparatively smooth with a ridge along the median line. During solidification gaseous matter seems to escape, and sometimes to cause the projection of small globules of metal into the air, in which case the upper surface of the ingot is rendered rough by numerous small irregular prominences formed by the exit of gas. When the upper surface of the ingot is smooth and presents a ridge, there is no projection of globules; but just at the moment of setting, a quantity of still liquid metal is squeezed out, producing the ridge. Although the escape of gas was not proved by its being actually collected, yet the appearances during solidification, and especially the structure of the ingots revealed by their fracture, leave no doubt of the fact. On the fractured surfaces of some ingots were observed numerous tubular cavities, which converged from the sides and bottom towards the centre of the upper surface, where many of them could be seen to terminate in little crater-like prominences. The metal forming the interior of these cavities was bright, and without the slightest appearance of tarnish by oxidation or otherwise. There were also innumerable smaller cavities visible only by the aid of a lens, under which the whole substance of the metal appeared vesicular. On the fractured surfaces of other ingots there were no large cavities, but the metal throughout was vesicular even to the naked eye. Between these two kinds of fractured surfaces every gradation may be met with. Those which presented the tubular cavities first described had a uniformly rough upper surface, whereas the upper surface of those which were free from such large cavities and more or less uniformly vesicular had a ridge, but was otherwise smooth. The specific gravity of one piece of a small ingot of the first kind was 8·211, and of another piece of the same ingot 8·285. The specific gravity of a small ingot of the last kind (with ridge) was 7·851.

3. When the same electrotype copper was melted under charcoal and poured through an atmosphere of coal-gas into a mould filled with the same gas, it solidified with a smooth and bright surface, and when fractured showed no trace of vesicular structure. Instead of a ridge on the upper surface there was a depression, accompanied with the same appearance of crystallization as when the metal is melted and allowed to solidify under charcoal. The experiment may be very easily made by directing a copious jet of flaming gas upon an open mould and then pouring out the metal in the midst of the flame. The fracture of an ingot of copper cast in this way is remarkable; it appears perfectly compact, and has a delicate, *pale* salmon-colour with a silky lustre. In order to succeed in casting the copper which has been melted under charcoal perfectly free from cavities, the utmost

precautions must be taken to exclude air. The method found to answer best was to place on the crucible a lid just large enough to cover it, and having two holes near its circumference. The mould must also be covered with a piece of sheet iron in which are two holes, one for the admission of the gas and the other for its exit. The melted copper must be poured through the escaping current of coal-gas into the mould through one of the holes in the lid of the crucible, so that any atmospheric air which enters through the other may be instantly deoxidized by the charcoal in the crucible. The difference occasioned by pouring the metal through an oxidizing medium like atmospheric air, or a reducing one like coal-gas, was observed many times, and it was found quite easy, by suitably arranging the moulds beforehand, to cast from the same crucible one ingot of copper which should be porous and, immediately afterwards, another which should be perfectly free from porosity. It should be stated that all these experiments were conducted only on a small scale. It was also found practicable to cast copper with a dense structure by placing fine charcoal powder in the ingot-mould and pouring the metal into the charcoal as close to the mould as possible. Porous and dense ingots notably differ in colour. This depends upon the angle at which the light falls upon the fractured surface. In certain positions the colour of the fractured surface of a porous ingot resembles that of a dense one, except that it has not a silky lustre. When, however, the fracture of the porous ingot is so placed that the light falling upon it may enter the small cavities and be reflected therefrom to the eye of the observer, a *deep* salmon-red colour is perceived, which the fractured surface of a dense ingot never presents in any aspect. The deep red colour is due to the repeated reflections which the light undergoes when incident on the surfaces of the cavities.

From the preceding experiments it may be inferred that the rising of the surface was essentially connected with the evolution of gas, and that the formation of this gas was the result of the action of atmospheric air upon the melted copper in its passage from the crucible to the mould. It might have been supposed that air had become as it were entangled in the copper in the act of pouring, and that its nitrogen, as it afterwards rose to the surface and escaped, caused porosity. But in that case it is reasonable to expect that a similar effect should be produced in a greater or less degree by pouring through coal-gas, which is not the fact. Moreover, in many instances the porosity was so uniform through the entire substance of the metal that it is scarcely possible to conceive that it could have been occasioned by the simple mechanical entanglement of a gas. Still, without the sure knowledge, founded on exact experiment, it cannot certainly be affirmed that because copper in a state of fusion does not take up carburetted hydrogen, it cannot take up nitrogen and evolve it during the act of solidification. No experiment has yet been made of pouring melted copper through an atmosphere of nitrogen. Admitting, however, that it has not this power, we are driven to the conclusion that the rising of the surface of the ingot and the evolution of gas are due to the action of

the oxygen of the air upon the melted metal during the time of pouring into the mould. In the case of absolutely pure copper the result of that action could simply be the formation of a small quantity of dioxide of copper, which would immediately dissolve in the melted metal. The experiment, however, of pouring pure melted copper through the air has not been tried, though the result would be decisive. But supposing, for the sake of argument, that such an experiment had been made, and that an ingot free from porosity had been obtained, then the only alternative is that the phenomena in question must proceed from the action of oxygen upon some impurities in the copper. Now it will be borne in mind that the electrotype copper which was used in the foregoing experiments, though pure as compared with ordinary commercial copper, nevertheless contained 0·05 per cent. of sulphur, which is equivalent to about 0·22 per cent. of disulphide. Sulphurous acid might thus be generated by the action of oxygen on the disulphide, and in its escape occasion the rising of the surface and the porosity of the metal. Again, should it hereafter be demonstrated that copper may, when melted under charcoal, take up carbon even in small quantity, carbonic oxide or carbonic acid would be formed by the action of oxygen upon the melted copper and produce the same mechanical effect as sulphurous acid. That oxygen should, as has been supposed, exist diffused, or, as it were, dissolved, in melted copper and be liberated during solidification, notwithstanding the strong affinity of copper for oxygen at high temperatures, requires to be established on much stronger evidence than has hitherto been advanced. The investigation is now reduced to narrow limits, and it is to be hoped that the remaining doubtful points will ere long be finally settled.

Copper and nitrogen.—The action of ammonia upon copper heated to redness has been investigated by several chemists, whose results differ in certain respects, but agree in the fact that the metal is rendered extremely brittle. On the one hand it was maintained that the copper only suffered an allotropic change, and that its weight remained the same, while, on the other hand, it was maintained that it absorbed nitrogen and increased proportionately in weight. Experiments which have been made upon this subject by A. Dick in my laboratory have led to the following results:—When electrotype copper wire free from dioxide of copper was heated to redness in a current of dry ammoniacal gas, it neither became brittle nor appeared to suffer any change whatever; but when commercial copper-wire, which always contains dioxide, was similarly treated, it became excessively brittle, its specific gravity was diminished, and water was formed. In one experiment wire which contained 0·17 per cent. of lead, but no antimony, was reduced in specific gravity from 8·733 to 8·64. When the same wire was melted in hydrogen or under charcoal so as to reduce the dioxide, then rolled out, and afterwards subjected to the action of ammonia at a red heat, it remained perfectly unaltered. From the preceding data it is inferred that the hydrogen of the ammonia induces brittleness in copper in the manner explained at page 267. It should, however, be stated that copper was rendered more brittle by being

heated in ammonia than in hydrogen or carbonic oxide, but the cause of this difference of action was not ascertained. Schrötter exposed very finely divided copper, which was prepared by reducing oxide of copper by hydrogen at the lowest possible temperature, to the action of ammoniacal gas at a red heat, and convinced himself that the metal underwent no chemical change.[4] As copper thus produced is free from dioxide, Dick's results agree with those previously obtained by Schrötter. This chemist succeeded in preparing a definite combination of copper and nitrogen, having the formula Cu^6N, by subjecting protoxide of copper to the action of dry ammoniacal gas at a temperature gradually raised to that of boiling linseed-oil. It was mixed with oxide of copper, which he was unable completely to separate. When exposed to a temperature somewhat below a red heat, it was decomposed with incandescence, nitrogen was evolved, and a mixture of metallic copper and dioxide remained. Some of this nitride of copper was examined by Berzelius, who described it as a dark olive-greenish powder, which on being rubbed on a touchstone gave a shining brass-yellow streak. The nitride was digested in a mixture of caustic and carbonate of ammonia, when a blue solution and an insoluble residue were obtained. This residue was washed with water; its volume was equal to that of the original nitride; when dried its colour was darker grey, and it detonated at a lower temperature than before the treatment with ammonia.[5] It does not explode by percussion.

Copper and phosphorus.—These elements readily combine at high temperatures. By carefully dropping phosphorus upon melted copper in a crucible, a product rich in phosphorus may be easily produced. In this way I have combined copper with as much as 11 per cent. of phosphorus, and I do not know whether the metal is not capable of taking up a still larger amount. Another specimen prepared by the action of phosphorus on heated copper-turnings contained 9·6 per cent. A small quantity of phosphorus does not sensibly alter the colour of copper, but a large quantity renders the metal grey. Copper containing only one half per cent. of phosphorus is very red, short, and cannot be rolled, except when cold or at a very slight increase of temperature, without cracking. By adding a little phosphorus to melted copper in a crucible the metal may be cast into a perfectly sound ingot, and marked contraction occurs during solidification. Phosphorus increases the fusibility and hardness of copper, and when present in large quantity renders it brittle at the ordinary temperature. The metal appears to be perfectly homogeneous. Copper containing 11 per cent. of phosphorus is extremely hard, and can scarcely be touched with a file. It is susceptible of a fine polish, but speedily tarnishes, at least in a London atmosphere. The colour is more or less steel-grey. When cast into a bell it gave a clear sonorous sound, which was inferior in quality of tone to a bell of the same dimensions consisting of 7 parts of tin and 24 of copper. When phosphorized copper is made by the direct addition of phosphorus to the melted metal, care should be taken

[4] Berzelius, Jahres-Ber. 1842, 21, p. 86.

[5] Jahres-Ber. loc. cit.

to stir either with a copper rod or a carbonized stick. On one occasion I used an iron rod, when I found that the metal contained a considerable amount of iron. It had the following composition:—

Copper	95·72
Iron	2·41
Phosphorus	2·41
	100·54

By digestion with *dilute* nitric acid an insoluble black powder remained, which was quite free from copper, and consisted of 0·93 of phosphorus and 1·99 of iron, so that it may be exactly represented by the formula Fe^3P^2. Notwithstanding the large amount of iron and phosphorus, the metal could be rolled cold and afterwards drawn out into tolerably fine wire.[6] The experiments on rolling and wire-drawing were made at a mill in Birmingham by regular workmen. Berthier states that "a very small quantity of phosphorus renders copper extremely hard and suitable for cutting instruments."[7] According to my experience copper containing ½, or even 2½, per cent. of phosphorus cannot be said to be extremely hard, though it may be sensibly harder than ordinary copper. Berzelius "saw a penknife of phosphide of copper which had the colour of copper, but gradually blackened in the air."[8] This statement rather surprises me, as I should certainly have expected that if the metal had been hard enough for a penknife, it would have contained sufficient phosphorus to render it grey. Several definite phosphides of copper have been prepared and described by H. Rose which have no special interest in a metallurgical point of view. They are easily decomposed by roasting.[9] The maximum amount of phosphorus which copper is capable of retaining at a high temperature is stated to be 7·7 per cent.,[1] whereas, according to Berthier, it is 20 per cent. When phosphorized copper is prepared by direct combination of the elements in the manner described, there is necessarily considerable loss of phosphorus by volatilization. The following experiments on the preparation of phosphorized copper have been made in the metallurgical laboratory.

1. By R. Smith. Phosphate of copper ($2CuO, PO^5 + aq$) was reduced by charcoal. The phosphate was prepared by adding common phosphate of soda to a solution of sulphate of copper.

Phosphate of copper (dry, but not ignited)	860 grains.
Charcoal	240 do.

An intimate mixture was made and exposed to a strong red heat. A brittle metallic button was obtained, weighing 200 grains; its fracture was largely crystalline and iron-grey.

2. By R. Smith.

Phosphate of copper (dry, but not ignited)	1000 grains.
Charcoal	200 do.
Starch	500 do.
Carbonate of soda (dry)	500 do.

[6] Chem. Gazette, v. 50, p. 1.
[7] Tr. des Essais, 2, p. 410.
[8] Tr. de Chimie, 2e éd. Française, 2, p. 534.
[9] Berzelius, op. cit.
[1] Ibid.

An intimate mixture was made and heated like the last. The product was a carbonaceous mass through which metallic globules were diffused. It was again heated, with the addition of 500 grains more of carbonate of soda, when a button and a few globules were obtained weighing together 210 grains. The button was somewhat crystalline on the upper surface, and in cavities on the under surface were small bright crystalline plates almost of the lustre of graphite; its fracture was coarsely granular, more or less porous, and nearly of the colour of white iron.

3. By A. Dick. A mixture of bone-ash, silica (sand), charcoal, and copper-clippings, was exposed to a white heat for about an hour, and a similar mixture without silica was heated at the same time in the same furnace. In both crucibles the product consisted of carbonaceous matter, through which metallic globules were diffused; some were grey and very brittle, while others were copper-coloured and malleable; they easily dissolved in nitric acid. Some of those prepared without silica were remelted; the button obtained was very hard, and sufficiently brittle to be easily fractured; the fracture was pretty even, very close-grained, and somewhat crystalline; it was found to contain a considerable amount of phosphorus.

Copper and arsenic.—Combination between these elements may be directly effected by dropping metallic arsenic into melted copper and stirring well, but not without considerable loss of the former metal by volatilization. When a small quantity of metallic arsenic is thus added to melted copper in a crucible the metal may be cast into a sound ingot, which contracts during solidification, as in the case of phosphorized copper, and may be rolled while cold without cracking at the edges and afterwards drawn out into fine wire. Copper may be easily combined with a large quantity of arsenic by heating it in admixture with arsenious acid and charcoal, or by heating an arsenite, or arseniate of copper, with charcoal. The following experiment was made by R. Smith with the proportions prescribed by Berthier.

Copper	500 grains.
Arsenious acid	1000 do.
Carbonate of soda	1000 do.
Starch	500 do.

An intimate mixture was made and exposed to a strong red heat. A metallic button covered with a little black slag was obtained weighing 760 grains; it was hard and brittle; the upper and under surfaces consisted of small clusters of crystals, and on the under surface were distinct acicular crystals; its fracture was somewhat crystalline and dark bluish-grey; it melted at a red heat before the blowpipe, and evolved copious fumes, smelling strongly of arsenic. Supposing the whole of the copper employed to have been present in the button, the increase due to arsenic is 34·2 per cent.; but this is somewhat below the amount indicated by the formula Cu^2As, which, according to Berthier, should represent the composition of the metal obtained from the mixture prescribed. The following statements are given on

the authority of Berthier. This arsenide of copper undergoes no change by exposure to the highest temperature, and when melted in any proportion whatever with copper the product is apparently homogeneous; not the smallest shot of copper separates. The metal produced by melting 1 part of the arsenide (Cu^2As) with 4 parts of copper is semi-ductile, reddish-grey, has a slightly fibrous fracture, and is susceptible of a very fine polish. It suffers no change when heated with alkaline carbonates or black flux. Nitre in fusion attacks it energetically and acidifies all the arsenic before it begins to oxidize the copper, so that, by employing a proper proportion of this salt, pure copper may be obtained from any arsenide of copper whatever. When copper containing arsenic is heated with oxide or arseniate of copper, arsenious acid is evolved, and by suitable mixtures of this kind the arsenic may be wholly expelled from copper. A mixture of 10 parts of arsenide of copper (Cu^2As) and 6 of protoxide (CuO) yields, when heated, 10·9 of copper; and a mixture of 10 of arsenide with 6 of arseniate of copper ($2CuO, As^2O^5$) yields about 9·2, provided always that the operation takes place in perfectly closed vessels. When fusion is effected in crucibles with access of air the arsenide is more or less roasted with the expulsion of much arsenic, and, consequently, less oxide or arseniate of copper is then required to render the copper pure. It has been found that by operating in crucibles on only 10 grammes of arsenide (Cu^2As), not more than 4 of protoxide, or 7 of arseniate of copper, are required to effect perfect separation of the arsenic.[2]

Protoxide of copper cannot exist at a red heat in combination with arsenious acid, which at this temperature reduces it to dioxide, with the formation of arsenic acid; the product of this reaction contains arseniate of dioxide of copper; it is very fusible, traversing crucibles more rapidly than melted litharge, and has a more or less deep red colour.[3]

Copper and silicon.—Copper containing silicon may be prepared by heating it to whiteness in contact with silica and carbon. The copper should be finely divided and mixed with a large excess of fine sand and charcoal, so that, when melted, it may remain diffused in globules through the mass. The mixture should be exposed during some hours to the highest temperature of a good air-furnace. When cold the shots of metal may be easily separated by sifting, or otherwise, remelted, and cast into an ingot. A considerable quantity of siliciuretted copper has been produced in the metallurgical laboratory by this process. At my request Messrs. Robinson and Cotton, the well-known bronze-founders of Pimlico, were so obliging as to cast in my presence a large medallion with some of this metal. The surface of the casting was good, but the metal required a higher temperature for fusion than bronze. Mr. Dick, who prepared the metal, found it to contain 1·82 per cent. of silicon, and to have a specific gravity of 8·70. It much

[2] Berthier, Tr. des Essais, 2, p. 410.

[3] Berthier, op. cit.

resembles gun-metal in colour, is tough, and much harder than copper. While cold it may be rolled and hammered out, but at a red heat it cracks immediately by this treatment. The hardness which it acquires by hammering is removed by annealing. By *dipping* in nitric acid it becomes black, but in a mixture of nitric and hydrofluoric acids it retains its proper colour. It tarnishes rapidly by exposure to the air. One specimen of siliciuretted copper which we prepared contained a much larger quantity of silicon than that of which the medallion was made. But the maximum of silicon which may be made to combine with copper by the method described has not been ascertained. I submitted a specimen containing 1·82 per cent. to Mr. Anderson, of the Gun Factory at Woolwich, who found it tougher than gun-metal. Copper much richer in silicon may be made by heating it in the form of powder or foil with silifluoride of potassium, or sodium, and metallic sodium. For this process we are indebted to Deville. The late Mr. Henry informed me that he found 10 or 11 per cent. of silicon in a specimen of siliciuretted copper which he obtained by this process. I have prepared the metal in considerable quantity by the same process, and in different experiments have obtained it varying in colour from yellow to greyish-white, according to the proportion of silicon with which it was combined. It is very hard, extremely brittle, and may easily be pulverized. Its fractured surface has a brilliant lustre, is more or less vitreous—resembling that of an alloy of 2 parts of zinc and 1 of copper—and speedily acquires a yellow tarnish by exposure to the air. It is more fusible than copper. It is readily attacked by nitric acid, strong or dilute, with the separation of dark-grey powder, and the solution gelatinizes by evaporation. A specimen which contained 5·2 per cent. of silicon was yellowish-white on the cut surface, which had considerable lustre. It was easily frangible. The fractured surface appeared manifestly crystalline under a lens; it was extremely hard to the file; it was more fusible than copper.

Specific gravity of copper.—There is considerable difference between the observations which have been published on the specific gravity of copper, and this is, no doubt, mainly to be ascribed to the difficulty of obtaining the metal free from cavities. Berzelius found the specific gravity of copper after fusion to be 8·83; that of the same copper when drawn out into a cylinder 2 lines in diameter to be 8·9463; and that of the cylinder when flattened in the direction of its length to be 8·9587.[4] Marchand and Scheerer have carefully investigated this subject and published the following results.[5] When copper was melted under fluor-spar, or a mixture of fluor-spar and glass, it was vesicular, and the fluxes were imperfectly fused; but when it was melted under a mixture of borax and glass, soda and glass, soda alone, soda and common salt, or common salt alone, it presented a good appearance, and the fluxes were well fused. The copper with the brightest and

[4] Tr. de Chimie, Paris, 1846, 2, p. 520.
[5] Journ. für prakt. Chem. 1842, v. 27, p. 193.

smoothest surface was that melted under a mixture of borax and glass. In three instances in which the purest Russian copper was melted under such a mixture, the metal, from its outward appearance, did not lead to the suspicion of the least internal vesicularity, and yet the respective specific gravities of the three specimens thus obtained were 8·089, 7·720, and 8·132. They were divided through the middle by means of a fine saw, and were then found to be full of cavities, which were accumulated especially towards the centre and close under the upper surface of each button, where there was a warty projection. As in all these experiments the copper had been rapidly cooled, three similar experiments were made in which the metal was very gradually cooled, and in which the fluxes employed were glass, a mixture of borax and glass, and common salt, respectively. The respective specific gravities of the buttons of copper were 8·762, 8·586, and 8·899. Slow cooling, therefore, so far as may be inferred from the first two results, tends to increase the specific gravity of copper. The button obtained by melting under salt was perfectly free from cavities or any warty projections. Marchand and Scheerer remark that the only flux with which they procured copper free from bubbles contained no oxygen, namely, common salt; and they suggest the possibility that the other fluxes may have yielded oxygen to the copper and have derived an equal amount of that gas from the atmosphere. They moreover assume that the cavities in copper are caused by the liberation of oxygen during, or at the moment of, solidification of the melted metal. The improbability of the liberation of oxygen from melted copper has, it will be remembered, been previously discussed. The escape of oxygen from melted silver at the moment of solidification affords no ground whatever for supposing that the same phenomenon may occur in the case of melted copper, because silver, at the temperature of its melting-point, cannot exist in combination with oxygen, and copper, when in a state of fusion, has a very powerful affinity for oxygen. The vesicularity of the copper which was melted under fluor-spar, a substance containing no oxygen, is accounted for by the fact that the flux was very imperfectly fused and did not prevent access of air. Six observations were made on the specific gravity of copper melted under common salt, four with copper precipitated from a solution of sulphate of copper (cement-copper), and two with the best quality of Russian copper. The results were respectively as follow:—8·899, 8·885, 8·907, 8·891, 8·891, and 8·921. The difference between these numbers is supposed to be due either to imperfect exclusion of the air or errors in the weighings, notwithstanding they were several times repeated. The highest number is regarded as the most correct. The average of all the numbers is 8·899.

Experiments were next made to ascertain the effect of great pressure upon the specific gravity of copper. Six specimens of wire, $0^m,006$ (0·24 in.) in diameter, were found to have the following specific gravities, 8·935, 8·933, 8·939, 8·933, 8·934; the average being 8·935. The six specimens of copper which had been melted under common

salt, and of which the specific gravities have been previously stated, were subjected to the pressure of a hydraulic press in an apparatus of steel resembling an ordinary steel mortar. The results are presented in the table subjoined.

Specific Gravity before compression.		Amount of pressure in Prussian pounds to the Prussian inch.	Specific Gravity after compression.
8·899	Precipitated.	100,000	8·919
8·885		150,000	8·928
8·907		300,000	8·931
8·891		100,000	9·922
8·891	Russian.	200,000	8·927
8·921		212,500	8·930

Hence it appears that the specific gravity of copper which has been melted is increased by great compression, but the increase is so small that it can scarcely be ascribed to any other cause than want of compactness in the melted copper, which, in spite of every precaution, can never be entirely prevented. Minute cavities which may thus exist in the metal are more or less perfectly closed up by great pressure, and, consequently, the specific gravity is proportionately increased. The highest number, 8·931, should be accepted as the most correct for the specific gravity of compressed copper.

The following observations were made to determine the effect of the process of wire-drawing on the specific gravity of copper. For this purpose the finest Demidoff copper,[6] which contained scarcely a trace of foreign matter, was employed, and the wire was drawn from a hammered cylindrical bar. After the first drawing a piece of the wire was cut off and the remainder drawn thinner; a piece was then cut off the second wire, of which the remainder was drawn out again; and so on until a sufficient number of specimens were obtained. The weighings were made at 18° C. and 752^{mm} bar.

		Diameter in millimetres.	Specific Gravity.
1.	Hammered bar	55	8·9353
2.	Do.	26	8·9445
3.	Wire. Before drawing it was annealed at a red-heat	22·2	8·9435
4.	Do.	19	8·9454
5.	Do.	15·9	8·9437
6.	Do.	13	8·9469
7.	Do. Before drawing it was annealed at a red-heat	11·2	8·9432
8.	Do.	10·2	8·9488
9.	Do. The wire was previously annealed at a red-heat	9·6	8·9391
10.	Do.	8·4	8·9459
11.	Do.	7·7	8·9438
12.	Do.	6·3	8·9450
13.	Do. The wire was previously annealed at a red-heat	5·5	8·9414[7]

The conclusions which Marchand and Scheerer have drawn from

[6] See article which follows on the Electric Conductivity of Copper, p. 287. Mr. Matthiessen has recently found a considerable amount of impurity in some of this quality of copper.

[7] No correction has been made for weighing in air.

these data are, that copper-wire somewhat increases in specific gravity the finer it is drawn out, but that there is no corresponding increase in its hardness. It will, however, be observed, that if any importance be attached to the third decimals in the table, the first conclusion is not satisfactorily established.

The specific gravity of unmelted electro-deposited copper prepared from a solution of sulphate of copper was determined. Four pieces of such copper, carefully selected, had the following specific gravities:— 8·914, 8·900, 8·905, and 8·843. The differences between these numbers may be explained by the fact that electro-deposited copper is porous in a greater or less degree. The specific gravity of electro-deposited copper after treatment in different ways has been examined in my laboratory by A. Dick, whose results are as follow:—

Piece of a vesicular ingot cast under ordinary conditions	8·535
Another piece of the same ingot	8·505
Unannealed wire, made from the same ingot	8·916
The same wire annealed	8·919
Piece of an ingot cast in a mould containing sufficient charcoal-powder to protect the surface of the copper from the action of the air	8·946
Another piece of the same ingot	8·952
Piece of another ingot cast in the same manner	8·922
Unannealed wire made from the last ingot	8·952
Unannealed wire made from copper which had been melted under charcoal and allowed to cool in the crucible	8·937
The same wire annealed	8·930
Piece of an ingot cast in coal-gas	8·948
Another piece of the same ingot	8·958

It will be remarked that the specific gravity of copper which has been melted under charcoal and cast with a porous structure is increased by the process of wire-drawing, so that it is nearly as high as that of wire made from copper which had been cast with a dense structure. The specific gravity of copper which has been melted under charcoal and cast with a dense structure is not increased by the process of wire-drawing, and the specific gravity of the wire drawn from such copper is nearly the same before as after annealing. The specific gravity of one specimen of copper which had been cast in coal-gas, namely 8·958, is sensibly higher than the highest obtained by Marchand and Scheerer, namely 8·952, which occurred in a specimen of copper-wire hammered out to the thickness of $0^{m},00015$ (0·006 in.).

The specific gravities of four specimens of crystallized native copper which had been carefully rolled out were found by Marchand and Scheerer to be 8·940, 8·935, 8·933, and 8·962. The last specimen was from Brazil, and contained a sensible quantity of foreign matter. It had the following composition:—

Copper	99·56
Silver	0·30
Gold	0·08
Iron	0·10
	100 04

The facts which have now been advanced seem to render it probable that copper does not suffer a permanent decrease in volume by compression, and that the observed variations in specific gravity were caused by the varying porosity of the metallic mass. Were it even possible to cast pure copper absolutely free from cavities, yet, if it contract during solidification after fusion, spaces must be formed in the interior of the metal, because the exterior first becomes solid, and in that state is able to resist the pressure of the atmosphere as the still liquid metal within gradually contracts and solidifies.

Since the above was in type Mr. Charles O'Neill has communicated a paper to the Manchester Philosophical Society (March 5, 1861) on the Changes in Specific Gravity which take place in Rolled Copper by Hammering and Annealing. His results are embodied in the following extract from the published Proceedings of the Society:—

"In the first series of experiments ten pieces of copper were cut from a sheet of the thickness of $\frac{3}{8}$ inch; the pieces weighed from 250 to 320 grains each; their mean density was 8·879. The pieces were then separately subjected to the action of a powerful compressing machine, acting on the principle of the *genou*, about fifty blows being given. The density of these hammered pieces showed a mean of 8·855, being a loss of 0·024. The same pieces were annealed by being placed in red-hot sand, and cooled slowly; when cleared from adhering oxide, the mean density was found to be 8·884, being an increase of 0·029 on the hammered pieces, and 0·005 on the original pieces. A second series of experiments, made with very great care, corroborated the first in the main points. The pieces were from another and better sheet of copper: ten pieces, weighing each from 420 to 520 grains, showed a mean density of 8·898, being hammered by the same machine; their mean density became 8·878, showing a loss of 0·020 by hammering; upon annealing in a charcoal fire, the mean density of five out of the ten pieces was 8·896, showing a gain of 0·018 upon the hammered pieces, and a loss of 0·002 upon the original. A third series of experiments upon the change of density in a bar of copper by successive hammerings showed a loss of density from 8·885 to 8·867."

The conclusion drawn by the author from these experiments is, that the specific gravity of best commercial rolled copper is, contrary to what might have been anticipated, sensibly diminished by hammering.

Electric conductivity of copper.—We are indebted to Matthiessen and Holzmann for the best investigation of this subject.[8] Their results will be found in the table subjoined: the conducting power of a hard-drawn silver wire is taken as the standard and as equal to 100.

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[8] On the Effect of the Presence of Metals and Metalloids upon the Electric Conducting Power of Pure Copper. Trans. Roy. Soc. April 26, 1860. On the Electric Conducting Power of Copper and its Alloys. By A. Matthiessen, Ph. D. Proceedings of Roy. Soc. Feb. 28, 1861.

Wires hard-drawn.	How prepared.	Conducting Power.	Temperature at which the observation was made.
1. Pure copper ...	Protoxide reduced by hydrogen.....	93·00	18°6 C.
2. do. ...	Electrotype copper, not melted	93·46	20°2
3. do. ...	Do. commercial, do.	93·02	18°4
4. do. ...	No. 3, after fusion in hydrogen	92·76	19°3
5. do. ...	No. 3, hydrogen passed through the metal while melted	92·99	17°5
	Mean of the 12 determinations from which the preceding numbers were deduced	93·08	18°9
	Extremes observed.....	92·22	at 19°3
	and	93·81	at 19°7
	The conducting power was found to be increased about 2·5 per cent. by annealing the wires.		
6.	Copper containing dioxide, of which the proportion could not be determined with accuracy..... Electrotype copper melted in contact with air	73·32	19°5
7.	Copper containing 2·50 per cent. of phosphorus	7·24	17°5
8. do.	do. 0·95 do. do.	23·24	22°1
9. do.	do. 0·13 do. do.	67·67	20°0
10. do.	do. 5·40 do. arsenic	6·18	16°8
11. do.	do. 2·80 do. do.	13·14	19°1
12. do.	do. traces do. do.	57·80	19°7
13. do.	alloyed with 3·20 do. zinc	56·98	10°3
14. do.	do. 1·60 do. do.	76·35	15°8
15. do.	do. traces do. do.	85·05	19°0
16. do.	do. 1·06 do. iron	26·95	13°1
17. do.	do. 0·48 do. do.	34·56	11°2
18. do.	do. 4·90 do. tin	19·47	14°4
19. do.	do. 2·52 do. do.	32·64	17°1
20. do.	do. 1·33 do. do.	48·52	16°8
21. do.	do. 2·45 do. silver	79·38	19°7
22. do.	do. 1·22 do. do.	86·91	20°7
23. do.	do. 3·50 do. gold	65·36	18°1
24. do.	do. 0·31 do. antimony and 0·29 do. lead	64·5	12°
25.	Electrotype copper, from a dense ingot melted under charcoal, and cast in coal-gas by Dick (see p. 276).	93·2	12°8
26.	do. from a porous ingot of the same copper as No. 25, but poured into a mould under ordinary circumstances.	94·8	13°
	According to Matthiessen the conducting power of pure copper would be 96·4 at 13°C.		
27.	Electrotype copper cemented with charcoal, and containing silicon and traces of phosphorus and iron. (See Dick's experiments, p. 270).....	62·8	13°
	do. do.	63·2	14°2

In the following table Mr. Matthiessen has given the relative conducting powers of various kinds of commercial copper, as compared with pure unmelted electrotype copper, which is taken as the standard and as equal to 100 at 15·5°C.[2]

[2] Report to the Submarine Cable Committee of an Investigation relating to the causes of the different Electric Conducting Powers of Commercial Copper, by A. Matthiessen.

Wires annealed.	Conducting Power.	Temperature at which the observation was made.
1. Spanish, Rio Tinto. It contained 2 per cent. of arsenic, besides traces of lead, iron, nickel, dioxide of copper, &c.	14·24	14°8 C.
2. Russian, Demidoff's make. It contained traces of arsenic, iron, nickel, dioxide of copper, &c.	59·34	12°7
3. Tough-cake, make not specified. It contained traces of lead, iron, nickel, antimony, dioxide of copper, &c.	71·03	17°3
4. Best selected, make not specified. It contained traces of iron, nickel, antimony, dioxide of copper, &c.	81·35	14°2
5. Australian, Burra-Burra. Traces of iron and dioxide of copper only were found	88·86	14°0
6. American, Lake Superior. It contained traces of iron and dioxide of copper, and 0·03 per cent. of silver	92·57	15°0

HISTORICAL NOTICES ON COPPER-SMELTING IN GREAT BRITAIN.

At present I am not in possession of sufficient materials to enable me to present a complete history of copper-smelting in this country. However, such information on the subject as I have been enabled to collect from various sources, I shall now introduce. I am informed by Mr. Albert Way and Mr. Franks, the eminent archæologists, that lumps of metallic copper, more or less rounded, have been discovered in different parts of the country, but always in association with articles of bronze. Mr. Franks showed me one of these lumps, which evidently had been melted, and which, on examination in the metallurgical laboratory, proved to be practically pure copper. Pennant describes a cake of copper found at Caerhun (also spelled Caer-hēn), the ancient Conovium, near Conway: it weighed 42 lbs., and in form resembled a cake of bees' wax; the diameter of the widest part was 11 inches, and the thickness in the middle 2¾; on the upper surface was a deep concave impression, with the words *Socio Romæ* (to my partner at Rome), and obliquely across these was impressed in smaller letters the inscription, *Natsol*. Caerhen is only a few miles from Llandudno, where ores of carbonate of copper continue to be raised to this day. The first inscription, and the occurrence of the lump in close proximity to mines yielding copper-ore of the most easily reducible kind, would lead us to conclude that this ore was melted *in situ* by the Romans.

In the time of Elizabeth there was a rich copper-mine at Keswick, in Cumberland, of which that Queen deprived the Earl of Northumberland on the ground that it was a mine-royal.[1] It is reported that not less than 4000 men were employed at this mine; but this is probably a great exaggeration. The ore appears to have been a sulphide; for Webster, the author of the 'Metallographia,' describes it as an ore "that must be often melted in the fire ere it be brought into the form of good copper." According to Camden, much good copper continued during a long time to be made at Keswick and Newland; but Webster, in 1671, wrote that "now the Work is quite left and decayed:

[1] Some Account of Mines, and the *Advantages* of them to the Kingdom. By Thomas Heton, M.A., Vicar of *Layston* in *Hertfordshire*, etc. London, 1707, p. 15.

yet I am informed that some do now melt forth as much very good copper as serveth them to make half-pennies and farthings."[2]

More ancient records of copper-mines exist: thus Edward III., in the fifteenth year of his reign, granted the right of working "the copper-mines of Skildane in Northumberland, and the copper-mine of Alston-Moor in Cumberland, and the copper-mine near Richmond in Yorkshire, during a term of fifteen years, and on payment of a royalty to himself of one-eighth, and one-ninth to the Lord of the Soil," to a company of adventurers, amongst whom his brother Richard, Duke of Gloucester, and Henry, Earl of Northumberland, are mentioned.[3] That the copper-ore which was raised in these earlier times was smelted at or near the mines, I think there is reason to suppose, notwithstanding the absence of any positive historical record of the fact. The Hindoos have smelted copper from time immemorial; and to this day conduct the operation in small blast furnaces about 3 feet high, with charcoal and cow-dung as the fuel. The ores which they employ are not those of the easily reducible class, such as carbonates, but sulphuretted ores, like copper-pyrites. But, if these rude tribes of mankind are able to smelt copper-ores with success, it is not difficult to believe that our ancestors, at least those of the fourteenth century, possessed an equal degree of metallurgical skill. Moreover, it appears certain that copper-ore was raised in this country many hundred years ago, and it must either have been smelted at home or exported; but I am not aware whether there is any historical evidence of the fact of such exportation: if not, we have an additional though negative argument in favour of the supposition which I have above ventured to express concerning the early history of copper-smelting in England. On the other hand it should be stated that our ancestors imported copper from Hungary[4] and Sweden, and allowed calamine to be exported as ballast.[5]

Copper-works were in operation in Yorkshire during the last century. Mr. Keates has communicated to me the following particulars on this point:—"Copper-smelting, I believe, was carried on in Yorkshire to a limited extent; but all that I know of it was told me by old Samuel Burgoyne in 1822, who at that time was eighty-four years of age, and was consequently born in 1738. His father worked at the copper-works at Middleton Tyas, in Yorkshire. He said: 'The ore was green and red, and melted by blast; the work stopped when I was about twelve years, and we came to live at Ecton.'" Mr. Keates has furnished me with a copy of a memorandum which confirms the preceding statement: "April 17th, 1752.—Essayed the sample of Middleton Tyas round ore brought me by Mr. Rotton's son. Quantity $13^{T.}\ 4^{C.}\ 2\ 13$ . . . . . 20 dwts. produce 9 dwts. of fine." This shows that the ore yielded 45 per cent. of fine copper. Jars states that in 1765 copper-smelting in this locality was effected in re-

[2] Metallographia, etc. By John Webster, etc. London, 1671, p. 244. I have cited Camden on the authority of Webster.

[3] Heton, op. cit., p. 9.

[4] See Specification of Patent to George Danby, A.D. 1636, Jan. 21.

[5] Heton, op. cit. pp. 153, 154.

verberatory furnaces, and that various kinds of ore were raised from the neighbouring mines, amongst which he mentions green carbonate of copper, vitreous-copper, and rarely yellow ore, or copper-pyrites.[6]

In Staffordshire copper-smelting was carried on at the village of Ellaston, near Ashbourne. The ore was obtained from the well-known Ecton mine in the vicinity. Specimens of this ore, which I have seen, consist of copper-pyrites in association with calc-spar. Plot, writing in 1686, informs us that when he visited Ecton, the mine had ceased to be worked, and that at the mills at Ellaston, where they smelted three kinds of ore, "all was out of order," the famous *wooden-bellows* that had no *leather* about them "having been carried away to Snelston, in Darbyshire," whither he went to see them. From this it is clear that the smelting was conducted in blast-furnaces.[7] According to Plot, the stoppage of the mine and smelting-works was on account of "*Copper* comeing cheaper from *Sweden* than they could make it here."

The working of the Ecton mine was resumed; and Mr. Keates informs me that about 1750 the ores raised from this mine were smelted at Whiston, and some of the copper was carried to a forge at Bosley, on the river Dane, near Macclesfield, where it was hammered out into pans, &c. Other Staffordshire copper-ores were smelted at Cheadle about 1780. Mr. Keates has also communicated to me the fact that copper-ore was raised at the Ribden mine, distant a few miles from Alton Towers, and smelted at a place in the vicinity named "Blazing Star," on account of the light emitted at night; so that a blast furnace was probably employed. The ore consisted chiefly of carbonate and oxide of copper. Webster states, on the authority of one Dr. Merrett, that a copper-mine existed at Wenlock, in Staffordshire.[8]

The following historical notice of copper-smelting in Lancashire has been kindly supplied by Mr. Keates:—

"The first introduction of copper-smelting into Lancashire was by the ancestor of the present Colonel Patten; the works were at Bank Quay, on the banks of the Mersey, near Warrington. The building of these works commenced in 1717 or 1718. The ores were principally Cornish and Irish, with small importations from the West Indies, and the British Colonies in North America; some also were got from Alderly Edge, Coniston, &c. These works were dismantled, I believe, about 1780. The next works in Lancashire were built very near Liverpool: the present Mersey Iron and Steel Works stand on their site. They were carried on by Roe and Co., who had a brass manufactory at Macclesfield. Cornish and Irish ores were smelted at these copper-works, which were discontinued about the year 1800. Next in succession were the works at St. Helens, and at Stanley, a few miles distant. These works were of considerable magnitude, and were established by the father of the late Lord Dinorben and his partners for smelting the ores raised at the Parys and Mona mines in Anglesea: I have not the exact dates; but I believe they were begun about 1780,

[6] Voyages Métallurgiques, 3. p. 72.
[7] The Natural History of Staffordshire. By Robert Plot, LL.D. Oxford, 1686.
[8] Op. cit., p. 244.

and discontinued between 1812 and 1815. Copper-smelting then ceased entirely in Lancashire, but was resumed in 1830, when the writer built works at Ravenhead, near the site of the old St. Helens' Works, primarily with the object of smelting the ore raised at the mines of General Bolivar in Columbia; the legislature having granted permission to import and smelt foreign ores in bond, on condition that the produce should be exported in the state of cake or ingot copper. The works at Sutton, near St. Helens, were also built by the writer shortly after those at Ravenhead; and these have been followed by others, so that at present the quantity of fine copper smelted from ore in Lancashire is probably not less than 6000 tons per annum. The principal ores smelted are from the West Coast of South America, Canada, Cornwall, Ireland, and Wales, together with the sulphides of low produce imported by the chemical manufacturers from Spain, Portugal, &c., who first extract the sulphur from them, and then turn them over to the copper-smelters."

In the last century copper-smelting was carried on in Gloucestershire, at Bristol, and other neighbouring localities; but I have not been able to ascertain when it was first established in this county, or when it was discontinued. Through the aid of Mr. George Grant Francis, of Swansea, I have had access to MSS. in which I have found some precise evidence on the subject: it is contained in a formal deposition, which I insert verbatim, and of which the object was to prove that the smelting of copper was commonly effected in blast furnaces, and coke used as the fuel. The original is not punctuated:—

"Copy.—Edward James of Lower Forrest in the County of Glamorgan copperman aged seventy-two years and upwards maketh oath that sixty years ago or thereabout he was employed in a copper-smelting work at Redbrook in the county of Gloucester under one Mr. Thomas Coster and that it was then in constant practice in the said copper work to make use of a blast-furnace for melting calcined copper ore with pit coal by which operation coarse copper was produced at the first smelting ready for the refinery and that his father Edward James now deceased was employed by the said Mr. Thomas Coster at Redbrook aforesaid upwards of thirty years at the said blast-furnace in making copper in the manner aforesaid as he believes and has often heard him declare and that in or about the same time at another copper work called Lower Redbrook situate near Redbrook aforesaid there was another copper work under one Mr. Chambers at which work it was also constantly practised to make copper in a blast-furnace with coked coal which blast-furnace this deponent hath so seen at work And this deponent on his oath also saith that upwards of fifty years ago he himself has worked at a blast-furnace in which copper was made and wherein coked coal was used at Landore in the said County of Glamorgan under Dr. Lane of the City of Bristol now deceased and under the late Robert Morris Esqre of Swansea now also deceased And this deponent on his oath further saith that so far from its being any new inventation to make copper by a blast-furnace and the use of cocked (*sic*) coal or charcoal it was the ancient method of making

copper and formerly most in practice And this deponent has himself also used some years ago peat both raw and charred in a blast-furnace for the purpose of making copper.

(Signed) "EDWARD JAMES.

"Sworn at Swansea this 23 day of January 178 (*sic*) the words upwards of fifty years ago being then interlined before me

"JN° BEVAN,

"One of his Majesty's Justices of the Peace in and for the said County of Glamorgan."

Jars published, in 1781, a description of the smelting of copper in the vicinity of Bristol. There were two works, to which the greater part of the ores raised in Cornwall were conveyed by sea. Reverberatory furnaces were used, of which there were not less than fifty in one of these works. The regulus preparatory to calcination was broken and ground under edge-stones by horses.[9]

Aikin, writing in 1797, states that at Amlwch port in North Wales, the poorest ores of the Parys mine, which yielded only from 1½ to 2 per cent. of copper, were partially smelted, so as to produce a regulus containing 50 per cent. of copper, which, together with the rich ores, was exported to Swansea. There were two companies, each of which had a smelting-house, in which were thirty-one reverberatory furnaces.[1]

Copper-works were established by the Union Company at Risca, near Newport, Monmouthshire, in 1807, and continued in work till 1817, when, the copper trade being much depressed, the smelters determined to reduce the number of works, and they accordingly drew lots to decide which works should be given up. The lot fell upon the Risca works, which were consequently abandoned, and the buildings have since been used as chemical works.[2]

We now arrive at the history of copper-smelting in South Wales. In Carew's 'Survey of Cornwall,' of which the first edition was published in 1602, is the following passage:—"Touching metals: Copper is found in sundry places, but with what gain to the searchers I have not been curious to enquire, nor they hasty to reveal; for at one mine (of which I took a view) the ore was shipped to be refined in Wales, either to save cost in fuel, or to conceal the profit."[3] From the evidence which I shall adduce, and for which I am indebted to Mr. G. F. Francis, it may be certainly concluded that the first copper-smelting works at Swansea were not erected until after 1720; and that anterior to this date copper-smelting works existed at Neath. The following interesting letter was written by Mr. Gabriel Powell (the father of the locally celebrated Gabriel who died about 1787) to Mr. Burgh, who,

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[9] Voyages Métallurgiques, 3. p. 222.

[1] Journal of a Tour through North Wales, etc. By Arthur Aikin, London, 1797, p. 133 et seq.

[2] I am indebted to Mr. Octavius Morgan for this information concerning the Risca works.

[3] Carew's Survey of Cornwall; to which are added notes illustrative of its history and antiquities. By the late Thomas Tonkin, Esq., and now first published from the original manuscripts by Francis Lord de Dunstanville, London, 1811, p. 21. See also the note p. xii. as to the date of the first edition.

according to Mr. Hooper, the agent of the present Duke of Beaufort, was the then trustee and head manager of the Beaufort family :—

"Dear Sir. I have been favoured with yo" togeather with one inclosed to James Griffith wch I delivered & he has returned an Answear in the same words as the Copy thereof hereinclosed wch will save me the trouble of writeing a great deal of what I thought it my duty to mencon to you in that affayre. I shall therefore only observe that it must be granted that the Duke by obliedgeing us in a pticular (Taken by others without makeing the least acknowledgem^{t} to his Grace) will gain considerably & if so I hope Mr. Beavans & myselfe will not be thought the worse of encourageing the undertakeing. It may be imagined from the trouble wee take in solliciting this affayre that our measures are entirely broak if wee are disappointed therein but if I may creditt our managers It will not be 10$^{£}$ a yeare losse or advantage to us. They give instances of several workes carryed on without watter but were it absolutely necessary there are other wayes to supply that defect with ab^{t} 40$^{£}$ mor expence wch were it to fall to my own share I should not value very much but what gives me the greatest uneasinesse is that a cunning crafty pson (I mean Mr. Popkins for I dare name him tho' he dare not avow his false as wel as sly insinuations now [*sic*: nor?] the 10th pte of his incroachm^{ts} upon my Ld Duke & his other neighbours) who has from the beginning opposed my Ld Duke & his interest should prevayle with that family (wch wee have served to the utmost of our power) to Deny us a favo^{r} wch tends to his Graces interest. I cannot imagine how he comes to be soe careful of the health of the inhabitants of Swanzey all of a suddain —he has opposed its welfare all that lay in him & p'ticularly in the contest between us & the out Burgesses of Loughor for wch reason (among others) wee refused to bring him in Alderman—Sil: Bevans & myselfe are much more concerned for the health of this place, ourselves & family (wch are numerous) live in it & wee are not soe necessitous or soe covetous that wee would endanger our healths for any considerations whatsoever. There are several copper workes near Neath, several inhabitants ab^{t} those workes & yet we doe not hear the least complaint of any unhealthinesse thereby, nay, I am told there is a copper worke in y^{e} the middle of Southwark—must ours be more unhealthy than those or Docto^{r} Lanes wch is surrounded with inhabitants, verry strange indeed & what wee never heard untill y^{e} last Letter. It was insinuated unto me (who has been at 150$^{£}$ ab^{t} my Garden) in order to divert me from this affayre that it would spoyle my Garden—but that I look upon as idle as the least of their ptences. There is but one wind in the 24 & that wch blows y^{e} the most seldom vizt N.N.E. that will blow upon any p,te of y^{e} Towne & y^{e} work being three fields distance from ye uppermost house in Towne I am wel satisfyed It will not affect us—But upon ye whole let ye consequence be what it will wee are determined to Goe on & think it very hard that the Inhabitants of this place should be debarred of seeking those advantages wch their situation intitles them to without being opposed by strangers whose Avarice would ingrosse all advantages to

themselves—had wee the happinesse to see you here I should hope to have this affayre Terminated in our favo[r] but since that is denyed us I do insist on y[e] p,mise to visit our friends in Breconshire—Col[ll] Vaughan, Major W[ms] & honest M[r] Will: Aubrey expect you—my house Pennant (wch I desire you will make y[e]) is within halfe a mile of Brecon. If you will lett me know y[e] time—I will be sure to be there to Receive you—I doe not doubt but Ned Catchmayd (m or w?) & Will: Edwards will attend you

I am,
worthy S[r]
y[r] most obliedged humble
Servant
GAB POWELL
29th Sept. 1720."

For
John Burgh, Esq att
Foy near Monmouth
These.

Three days before the date of the preceding letter, the municipal authorities of Swansea had formally sanctioned the erection of copper-smelting works within the precincts of the borough. This sanction is contained in the following document, which cannot now be found, and to which, according to Mr. Francis, there is no reference in the Hall Book:—

"Wee the Portreeve, Aldermen & Burgesses of the Burrough of Swansey in the County of Glamorgan doe hereby certifye all whom it may concerne That wee doe approve of the erecting of a Copper Worke upon the Bank commonly caled (*sic*) M[r] Ley's Alias Thomas Evans Coale Bank and wee doe further Declare that it is our unanimous opinion that the Carrying on the said Worke will prove very much to the advantage and not in the least prejudicial or Hurtful to our said Burrough or the Inhabitants thereof. In Wittnesse whereof wee have hereunto sett our hands & the Common Seal of the said Burrough this 26th Day of September. Anno: Dom: 1720."

On this document is the following remark by the before-mentioned Gabriel Powell:—

"Since y[e] last Lre (letter?) y[e] Portreeve Aldermen (except Al[n] Ayres *who is steward to Mr. Popkins*,—Jenkin Jones whose sonnes in Law are imployed in bringing D[r] Lane's Oars & M[r] Da: Tho[s] who is p,missed to succeed in y[e] Dukes affayres) & Burgesses have putt their names & y[e] Comon (*sic*) Seal of the Burrough to an instrum[t] a Copy whrof is above written. G. P."

The site referred to in the preceding document is, according to the late Mr. Dillwyn, that on which the Cambrian Pottery-Works are now situated.

In George the Third's collection of topographical engravings in the British Museum I have found a curious old Indian ink drawing of copper-works at Llangefelach, the parish adjoining Swansea; and though I do not know when they were erected, yet it will be shown in the sequel that they were in operation in 1745.

From the evidence which has now been advanced we may, I. think, conclude with certainty that copper-smelting had been extensively carried on at or near Neath for a considerable period before it was established at Swansea; but I have not yet succeeded in obtaining more precise information on this subject. Carew, however, it will be remembered, states that copper "was refined in Wales;" and as this statement was published in 1602, there can be no doubt that copper-smelting was in operation in the Principality before that date. The term *refined*, in the passage quoted from the 'Survey of Cornwall,' is evidently used as synonymous with our present word *smelted*. Hence, unless it can be shown that when Carew wrote, copper-smelting was conducted in other parts of Wales, we may reasonably infer that the art had attained a considerable degree of development at or near Neath at least 120 years prior to its introduction into Swansea. It must be left to future antiquarian researches to elicit more precise evidence on this subject than we at present possess.

In Cornwall during the last century several unsuccessful attempts were made to smelt copper, of which a record has been preserved by Tonkin; and as the history of these failures may convey an important lesson to persons engaged in mining adventures, I insert this record without abridgment: it is contained in Lord de Dunstanville's edition of Carew's 'Survey of Cornwall,' and was evidently prepared in 1739 with a view to publication:[4]—

"This variety of ores and great increase in the mines has occasioned the setting up of six several companies for the buying of the ore, but who take care to keep us as much in the dark as they can, by shipping off all the ore to be smelted in their houses near Bristol, in Wales, &c., under a pretence of saving cost in fuel, but in reality to conceal the profit, as Mr. Carew very justly observes; so that we must be entirely at their mercy, as not understanding the true value of the commodity ourselves; or, if we did, they know that it would require a greater purse than any one private gentleman can be supposed to be enabled to lay out. It was, however, attempted about thirty years since by the late John Pollard, Esq. and Mr. Thomas Worth, jun. at St. Ives; and before them by Mr. Scobell, at Pol Ruddan, in St. Austell, with whom the late Sir Talbot Clarke and the old Mr. Vincent joined, and where the first piece of copper that ever was so (*sic*) in this country was smelted, refined, and brought to perfection. But both these attempts failed of success, more through ill-management, roguery of the workmen, and the ill-situation of the said smelting-houses, than any defect in the ore, or charge of the fuel. Since this, one Gideon Collier, of St. Piran in the Sands, erected an house for the like purpose at Penpol, in the parish of Phillack; but being soon taken off by a fever, in the best of his time, when he had made a fair progress in it, the same was carried on by the late Sir William Pendarves and Robert Corker, Esq. who have (particularly the last, with whom I have often discoursed about it) assured me that they could smelt their ore as

[4] P. 22.

cheap there, all hazards considered, as the companies could pretend to do at their houses in Wales, &c., and did so accordingly for some years. But they being both since dead, and their affairs falling into such hands as had other interests to mind, this project too sunk with them. A small beginning was also made to the same purpose at Lenobrey in St. Agnes, where they smelted some pieces of copper with good success; but were forced to give it over for want of a sufficient stock to go on with it. From all which essays, and some observations I have made of my own and gathered from some workmen abroad (but chiefly from the late Mr. John Coster, who owned to me that most of our ores might be smelted rough here as cheap as abroad, but not brought to the true fineness (for what reasons you may easily guess), and therefore must be shipped off to be refined), I am fully convinced that the ore may be smelted here, and refined too (that pretence being a mere cant, to conceal the real value), all things considered, at as small an expense as it can be done in Wales, &c. And if we allow for the great salaries the said companies are obliged to give to their agents here and elsewhere; the great charges they are at in working the mines (which they covet at any rate to get into their own hands); the hazard of the ore on shipboard, especially in time of war; and many other incidents, which would be saved if the ore was smelted here: I believe it would amount to a demonstration, that it would even be done much cheaper, in some convenient places in this county, than in Wales, &c. What advantage from this would accrue to our country in general, is too obvious to need any more words: and this the copper companies know but too well; and therefore keep us as much . . . . . [left unfinished by the author.]"

In 1754 copper-works were erected at Entral, in the parish of Camborne, and afterwards removed to Hayle, where coal could be procured at a less cost. According to Price "the [copper] companies left no method unsought to traduce the credit and stab the vitals of this undertaking. Threats and remonstrances were equally used to oblige or cajole the owners of the mines to abandon or suppress the new company at Hayle. The opponents of this association, using every expedient to mortify the spirit of this arduous undertaking, alternately raised the price of copper-ores and lowered the value of fine copper, to the great loss of the contending parties; which will ever be the case where monopolies are disturbed and the almighty power of opulence can prevail. But happening to have men of fortune and capacity at their head, they were founded in prudence, and withstood the shocks of power and artifice."[5] The same author informs us that copper-works were subsequently erected at North Downs, in Redruth; but the locality proving unsuitable, they were removed to Tregew, on a branch of Falmouth harbour, where they were carried on with advantage.

From the language of these writers, it is evident that the Cornish mine-adventurers considered themselves the victims of a conspiracy on the part of the Welsh copper-smelters. But it is difficult to under-

[5] Mineralogia Cornubiensis. London, 1778, p. 279.

stand why copper-smelting should have ceased in Cornwall if it had really been so profitable as Price declares. In one instance, at least, failure was not due either to deficiency of capital or incapacity in the management. As the adventurers felt themselves so much aggrieved by the smelters, they might have entered into a combination to keep up the price of copper-ore. Of all facts, none are more stubborn than those of political economy; and the truth of the matter appears to be, that copper-smelting can be conducted with greater profit in Wales than in Cornwall; and, therefore, it has become extinct in the latter county. When a man has an article for sale, he ought to know how much it has cost to produce it, and to fix such a price upon it as he considers remunerative. So, the miner should determine the value of the ore which he raises irrespective of the profit which it may subsequently yield to the smelter; and he has no right to impute injustice to the smelter who declines to inform him of the gains arising from the metallurgical treatment of the ore and to allow him to participate in those gains, which often entirely depend upon the exercise of individual skill and the possession of sound commercial knowledge. Whatever the profits of copper-smelting may have been in former times, it is certain that the smelters of the present day do not, in general, realize more than they are fully entitled to expect.

The last county to be mentioned in which copper-smelting has been conducted is Middlesex. About fifteen years ago works were erected on Bow Common for the purpose of smelting copper by a process devised and patented by Mr. James Napier, which will be described in the sequel. The locality was not suitable, and, as might have been anticipated, the works were speedily adandoned. The chief promoter of the undertaking was, I believe, the late Mr. Benjamin Smith, the silversmith, of Duke Street, Lincoln's Inn Fields.

Towards the end of the last century, probably between 1780 and 1790, copper-smelting was carried on at Ballymurtagh, Wicklow, Ireland. Through the kindness of Mr. Moyle, of Chatham Dockyard, I have received the following information on this subject from Mr. Edward Barnes, the present resident director of the Ballymurtagh Mines, now worked by the Hibernian Mining Company. Mr. Barnes writes that "when we first commenced the mine, none of the persons employed at the works were living, or at least remaining in the neighbourhood, and no records are to be found in the office of the Hibernian Mining Company on the subject. I think I have heard it stated that the smelting-works were erected by English parties, the Mining Company selling them the ore as raised. At the period referred to I rather think a considerable export duty was levied upon copper-ores, which, added to the low produce of the ore of Ballymurtagh and its high percentage of sulphur, were the chief causes of erecting smelting-works near the mine. An attempt was also made to save the sulphur by calcining the ores in rude kilns in the open air, the sulphur-fumes being received into long horizontal flues. This process was very slow and unsatisfactory, and there is reason to believe the Company were losers by it. Judging from the cleanness of the slag at Ballymurtagh

and at Arklow, it would appear that the process was well carried out and no copper left in it; but no doubt there must have been great disadvantage in operating upon one stubborn class of ore. The Company had a patent for coining their own copper tokens, as had also the Associated Irish Mining Company at Crenebane, who tried smelting on a smaller scale. This, I believe, was a general medium of payment with similar companies at the period."[6]

It would be difficult to select in this country a more eligible site for copper-smelting works than Swansea, and this for two reasons. The first is, that it is a good seaport, which is only at a short distance from Cornwall and Devonshire, the two counties in which the greatest amount of copper-ore is raised, and it is also easily accessible to vessels conveying ore, or products containing copper, from South America, Australia, and other parts of the world. The second is, that extensive collieries exist in the immediate vicinity, from which an abundant supply of coal can be obtained at a low price. Many of the smelters are themselves engaged in the working of collieries, and are thereby enabled to dispose of their coal to the greatest advantage, the large being sold at a good profit, either for home consumption or exportation, and the small, which is often very *dirty* from an admixture with shale, being reserved for the copper-furnaces. It is advantageous, both for the mine-adventurers and the smelters, that the process of smelting should be carried on in a locality where copper-ores of various kinds may be procured, for it is well known that frequently copper can be extracted at a less cost by smelting several ores in admixture than by smelting any one ore by itself. An illustration will make this point plain. Suppose we have two kinds of very poor ore, one consisting almost wholly of oxide of iron and the other almost wholly of quartz. It might not be profitable to smelt either separately; for, in the case of that of oxide of iron, it would be requisite to add quartz as a flux, and; in the case of that of quartz, it would be requisite to add oxide of iron as a flux. But it might be profitable to smelt the two ores together, as one would then serve as a flux to the other, and each would yield copper. This is not an imaginary case. The smelter, by having at command a variety of ores, may render an ore profitable which otherwise would have no value. Adventurers in copper-mines would do well to consider this matter, and to be cautious how they embark capital in the erection of smelting-works which can only derive a supply of ore from some one particular mine. However, I do not mean to assert that particular copper-ores cannot be smelted with profit. The advantages which Swansea possesses as a site for copper-smelting are shared in a greater or less degree by other localities in the vicinity, such as Neath and Llanelly. The copper-works near the Lancashire coast may be well situated for the importation of ores, for the exportation of copper from Liverpool, and for supplying the great local demand in Lancashire and the West Riding of Yorkshire; but they cannot obtain coal at the same price as Swansea and its neighbours. The

[6] MS., Avoca Lodge, Avoca, May 9th, 1861.

Swansea smelters enjoy the privilege of pouring dense volumes of thick sulphureous and arsenical smoke from comparatively *low* chimneys into the atmosphere, and destroying vegetation with impunity, for a considerable distance round. This privilege has now in the lapse of time become an established right, which would not readily be conceded in many other parts of the kingdom. The inhabitants of Swansea generally seem to be habituated to the inhalation of the smoke, and to submit to the evil, if evil it be regarded, with unmurmuring resignation.

Description of the mode of dressing and sampling copper-ores in Cornwall.—I am indebted for this description to my former pupil, Mr. Pearce, of the Royal Institution, Truro.

The ores consist chiefly of copper-pyrites, intermixed with small quantities of other cupriferous minerals, iron-pyrites, and the constituents of the vein in which the ore is found.

The ore is drawn from the shaft to about 30 feet above the surface and taken in waggons to an adjoining dressing-floor, where it is allowed to fall from this height on two rows of inclined bars, by which means it is separated into three divisions or sizes, called *rocks*, *roughs*, and *smalls*, for convenience of dressing. In the first, or top row of bars, which separates the *rocks*, the bars are 4 inches apart; and in the second row, which divides the *roughs* from the *smalls*, they are $1\frac{1}{2}$ inch apart.

The *rocks* are broken, by a process called *spalling*, into pieces of about one pound weight each. A small hammer, called sledge, is used in this operation, which is conducted generally by girls, who carefully separate the ore from the refuse. The richest part of the selected ore, termed *prills*, is taken, without any further preparation, to the crusher, which consists of two iron cylinders, or rolls, revolving against each other. They are worked by steam or water power, and between them the ore is passed, and reduced to a size small enough to pass through a sieve divided into holes of $\frac{1}{2}$ inch square. The preparation of the ore is now completed. The poorest part of the ore selected from the *rocks*, called *dredge*, containing from 10 to 20 per cent. of copper disseminated through a large bulk of matrix, is also crushed and passed through a sieve of holes about $\frac{1}{4}$ inch square. This prepares it for what is called *jigging*, of which the object is the separation of the ore from its matrix. The ore is put into a sieve of holes $\frac{1}{6}$ inch square, suspended in a large cistern of water. An up and down motion is then communicated to it by a break-staff, or lever, worked either by girls or by steam or water power. By this operation the lighter particles or refuse, on account of their less specific gravity, rise on the top, and are carefully skimmed off with a small wooden scraper. The ore that passes through, together with what stands in the bottom of the sieve, is then ready for the market.

The *roughs* from the second row of bars are placed under a stream of water to clean the ore from all extraneous matter, so that the copper-ore may, from its colour, be readily distinguished from the refuse, which is easily separated by what is termed *hand picking*, an operation conducted by girls who sit on tables near the stream. The picked ore,

by this operation, is divided into *prills* and *dredge*, and treated by the methods before described.

The *smalls* from the first separation are thrown on a griddle or sieve of holes ½ inch square; the coarse or larger particles which do not pass through are subjected to precisely the same treatment as the *roughs*, and the fine or smaller particles, if rich, are ready for the market, but if poor they are *jigged* through a sieve of holes ¼ inch square, preparatory to sampling.

The *prills* and *smalls* are then carefully mixed together into one pile or parcel, the *dredge* usually forming a separate parcel. The pile is then equally divided into 4 or 6 sub-piles, or *doles*, the number being regulated by the weight of the parcel; if above 20 tons it is divided into 6 *doles*, and if below that weight into 4 only. This division into doles is effected by means of a measure called *barrow*, which when exactly filled with the ore weighs about 1½ cwt. The number of *barrows* is carefully noticed, and, the exact weight of one being ascertained, a rough estimate of the total weight of the parcel can then be arrived at for the ticketing or sale. The parcel is now ready for sampling, which is conducted in the following manner:—

The Company's agent or sampler goes to the mine about a fortnight before the time appointed for holding the ticketing or sale, and selects two of the *doles* of the parcel; these, called the *sampling doles*, are then cut through or divided each into two parts, the division being about 12 inches wide. The sampler then takes down from the sides of the divisions about 1 cwt. of each dole, which is taken to the sampling-house, and there carefully mixed by him. A portion of it, about 30 lbs. weight, is then passed through a fine sieve, and again mixed by hand and put into as many small bags, holding about 1½ lb., as there are smelting companies—of which the number at present is 13—and one bag is also filled for the mine. The samples are then sent by the sampler to the companies' assayers, whose business it is to ascertain the quantity of fine copper in the sample according to the Cornish method of dry-assaying, and, according to the produces of copper found, the different companies fix the prices per ton they will offer for the parcel at the approaching sale or ticketing.

The sale of copper-ores.—Originally the Cornish miners disposed of their copper-ore by private contract; and, according to Price, at the end of the 17th century gentlemen from Bristol purchased it for 2*l.* 10*s.* to 4*l.* per ton. In about 1720 other gentlemen of Bristol entered into "a covenant with some of the principal miners of Cornwall to buy all their copper-ores for a term of years at a stated low price, particularly with Mr. Beauchamp to buy all the copper-ore which should rise out of a mine stocked for 20 years at 5*l.* per ton, and ore from other mines at 2*l.* 10*s.* per ton."[7] In about 1730 a gentleman from Wales visited Cornwall and purchased, at the rate of 6*l.* 5*s.* per ton, ready money, 1400 tons of copper-ore which had been lying unsold during some

[7] Mineralogia, p. 286. I derive my information of the early history of the copper-ore trade of Cornwall chiefly from this work.

years, and for which previously only 4*l.* 10*s.* had been offered. The Welsh visitor bought 900 tons more at 7*l.* per ton; and in the course of six months, before he left Cornwall, he purchased 3000 tons, upon which, Price informs us, he deservedly made very little, if at all, short of 40 per cent. profit. Soon afterwards it was agreed between the miners and smelters that the latter should, at stated periods, tender for the ores which might be ready for sale. At the appointed time and place of sale the agents of the smelters assembled, and a person was appointed on behalf of the miners to conduct the proceedings. Each agent delivered a paper, or *ticket*, upon which were written the name of the smelter, or company of smelters, and the sum tendered. The papers were then read aloud by the president, who declared the ore sold to the highest bidder. With the exception that in Cornwall the results of the sale are read by a clerk, the same mode of proceeding is practised to this day, and the places of sale now are Swansea, Truro, Redruth, Pool, and Camborne. The first sale of ore by ticketing at Swansea took place May 14th, 1804, when 52 tons of ores from North Wales were disposed of. In former times Price states, that "on this ticketing-day a dinner almost equal to a City feast was provided at the expense of the mines in proportion to the quantities of ores each mine had to sell." Until quite recently the ticketing-day at Swansea was celebrated by a dinner, but now the sale takes place early in the day and no refreshment of any kind is supplied. However, the *good old custom* is still maintained as a sacred institution in Cornwall; not, it is reported, with the willing concurrence of the mine-adventurers, who defray all the expenses of the *treat*, but for the special gratification of the smelters' agents, who, doubtless, like some other philosophers, consider it wise to season business with pleasure. When the same sum is offered by two or more smelters for a parcel of ore, it is equally divided between them. Each smelter has printed ticketing-papers with his name thereon. I subjoin a specimen of one in use at Swansea.

Ores for Sale, 186 .

Mine.	*No.*	21 *Cwts.*	*Price.*	
				Per 21 Cwts. Dry Weight.

FOR COPPER COMPANY.

Immediately after the sale the results are printed in a tabular form and distributed. When at Swansea in 1859 I attended a sale, after which the following table appeared:—

SWANSEA COPPER ORE CIRCULAR.—SEPTEMBER 6th, 1859.

Registered for transmission abroad.

Copper Ores, Sampled August 17th, and Sold at SWANSEA, September 6th, 1859.

MINES.	21 Cwt.	Produce.	1 Copper Miners' Co.	2 Freeman and Co.	3 P. Grenfell and Sons.	4 Crown Copper Co.	5 Sims, Willyams, Nevill, Druce, and Co.	6 Vivian and Sons.	7 Williams, Foster, and Co.	8 Mines Royal Co.	9 British and Foreign Copper Co.	10 Mason and Elkington.	11 P. Bankart.	12 Charles Lambert.	13 Ravenhead Copper Co.	14 Britonferry Copper Co.	Exceas.	Amount of each Parcel.	Amount of each Mine.
			£. s. d.	£. s. d.	£. s. d.	£. s. d.	£. s. d.	£. s. d.	£. s. d.	£. s. d.	£. s. d.	£. s. d.	£. s. d.	£. s. d.	£. s. d.	£. s. d.	s. d.	£. s. d.	£. s. d.
1 Cobre *Augusta Schneider*	80	13	12 0 0	11 18 0	12 6 0	12 0 0	12 7 0	12 10 0	12 1 0	12 4 0	11 11 0	12 0 0	12 11 6	12 0 0	12 0 0	11 15 0	1 6	1066 0 0	
2	79	13	12 0 0	11 18 0	12 6 0	12 0 0	12 11 0	12 9 0	12 2 0	12 4 0	11 11 0	12 0 0	12 9 6	12 0 0	12 0 0	11 15 0	1 6	991 9 0	
3	78	13	12 0 0	11 18 0	12 6 0	12 7 0	12 7 0	12 8 0	12 10 0	12 4 0	11 11 0	12 0 0	12 2 6	12 0 0	12 0 0	11 15 0	2 0	975 0 0	
4	77	13	12 5 0	12 0 0	12 8 0	12 7 0	12 1 0	12 10 0	12 10 6	12 2 0	12 0 0	12 5 0	12 5 6	12 6 0	12 0 0	12 0 0	0 6	964 8 6	
5	74	13	12 9 6	12 0 0	12 11 0	12 0 0	12 1 0	12 10 0	12 2 0	12 2 0	12 0 0	12 5 0	12 5 6	12 6 0	12 0 0	12 0 0	1 0	928 14 0	
6	71	13	12 9 0	12 11 6	12 11 0	12 0 0	12 1 0	12 10 0	12 2 0	12 2 0	12 0 0	12 5 0	12 5 6	12 12 0	12 0 0	12 0 0	0 6	894 12 0	
7 *Leon Raymundo ex R. E.*	89	12	11 18 0	11 15 0	11 18 0	11 17 0	11 11 0	12 1 0	12 0 0	12 3 6	11 11 0	11 13 0	12 2 6	11 11 0	11 10 0	11 0 0	1 0	1083 11 6	6843 15 0
8 Cuba.....*Mangosteen*	102	13	11 4 6	11 5 0	11 7 0	11 0 0	11 2 0	11 10 0	11 3 0	11 4 0	11 0 0	11 7 0	11 5 6	11 7 0	11 0 0	11 5 0	3 0	1173 0 0	
9	95	12	11 0 0	11 7 0	11 5 0	10 17 0	10 15 0	11 4 0	11 0 0	10 16 0	10 16 0	11 0 0	11 3 6	10 14 0	10 12 0	11 5 0	2 0	1078 5 0	
10	92	13	11 8 0	11 0 0	11 2 0	11 0 0	10 17 0	11 7 0	11 3 6	10 16 0	11 0 0	11 2 0	10 15 6	10 14 0	10 15 0	11 5 0	1 0	1048 16 0	
11	60	22	20 9 0	9 18 0	20 10 6	20 0 0	19 10 0	20 3 0	20 5 0	19 16 0	19 10 0	19 9 0	20 1 6	19 0 0	19 12 0	18 10 0	5 6	1231 10 0	
12	4	34	30 0 0	30 10 0	30 0 0	29 15 0	31 6 0	31 4 0	30 0 0	30 14 0	29 12 0	29 18 0	30 15 6	29 0 0	30 10 0	31 17 6	11 6	127 10 0	
13 Precipitate S.J.M.	4	71	60 0 0	57 0 0	60 0 0	54 0 0	65 0 0	65 11 0	55 0 0	60 0 0	59 0 0	50 0 0	65 13 6	60 0 0	60 0 0	64 19 6	2 6	262 14 0	
14 A.V.E.	4	73	61 0 0	58 0 0	60 0 0	54 0 0	67 6 0	67 18 0	55 0 0	62 0 0	60 0 0	50 0 0	66 13 6	60 0 0	62 0 0	67 9 0	9 0	271 12 0	5193 7 0
15 Parys.....*Good Intent*	151	4	3 15 0	3 10 0	4 0 0	3 12 0	3 15 0	3 15 0	3 14 0	3 10 0	3 10 0	3 10 0	3 17 6	3 18 0	3 8 0	3 5 0	2 0	604 0 0	
16 *Mary Hannah*	125	4	3 15 0	3 10 0	4 1 0	3 12 0	3 15 0	3 15 0	3 14 0	3 10 0	3 10 0	3 10 0	3 12 6	3 17 0	3 8 0	3 5 0	4 0	506 5 0	1110 5 0
17 Knockmahon *Sea Bird*	82	10	9 0 0	9 0 0	9 10 0	9 8 0	9 5 0	9 12 0	9 10 0	9 2 0	8 16 0	9 5 0	9 5 6	9 5 0	9 0 0	9 0 0	2 0	787 4 0	
18	42	10	8 17 6	8 8 0	8 18 0	8 17 0	9 1 0	8 18 0	8 19 0	8 9 0	8 10 0	8 12 0	8 17 6	8 12 0	8 5 0	8 3 0	2 0	380 2 0	
19	41	8	8 2 6	8 0 0	8 11 0	8 10 0	8 11 6	8 12 0	8 12 0	8 4 0	8 0 0	8 5 0	8 0 0	8 6 0	7 18 0	7 10 0	..	352 12 0	1519 18 0
20 Bearhaven.....*Allihies*	118	9	8 0 0	7 15 0	8 0 0	8 5 0	7 17 0	8 4 0	8 7 0	7 16 0	7 15 0	7 15 0	8 6 6	7 15 0	..	7 15 0	0 6		985 6 0
21 Spanish Ore. *Farmouth*	110	11	6 0 0	6 0 0	6 6 0	6 2 0	6 6 0	6 14 0	6 4 0	6 0 0	5 15 0	6 8 0	6 5 6	..	..	6 0 0	0 6	737 0 0	
22	1	17	15 0 0	14 10 0	16 10 0	15 17 0	18 1 0	17 0 0	16 0 0	16 10 0	14 14 0	16 0 0	15 10 6	..	..	16 0 0	21 0	18 1 0	
23	2	31	25 0 0	24 10 0	26 0 0	24 17 0	27 10 0	26 0 0	25 0 0	26 0 0	24 0 0	24 0 0	25 12 6	..	..	23 10 0	30 0	55 0 0	810 1 0
24 Spanish ..	12	5	4 0 0	4 5 0	4 4 0	4 8 0	4 19 0	4 19 0	4 10 0	4 0 0	3 10 0	..	4 10 6	..	..	3 10 0	..		59 8 0
25 Wildberg ....*Sovereign*	7	14	12 5 0	11 18 0	12 15 0	12 8 0	12 18 0	12 18 0	12 10 0	11 11 0	12 0 0	..	11 10 6	..	..	13 0 6	2 6		91 3 6
26 English & Canadian..	3	34	30 10 0	30 15 0	30 10 0	30 7 0	32 7 0	30 0 0	30 10 0	30 10 0	30 0 0	29 10 0	31 16 6	..	..	32 11 6	4 6	97 14 6	
27 ..	2	25	23 0 0	22 10 0	22 10 0	21 15 0	23 12 0	23 0 0	22 0 0	22 10 0	22 0 0	21 10 0	22 16 6	..	..	24 0 0	8 0	46 0 0	
28 ..	2	36	32 0 0	31 10 0	31 10 0	30 18 0	33 6 0	32 0 0	31 0 0	30 15 0	31 0 0	30 0 0	32 16 6	..	..	33 13 6	7 6	67 7 0	213 1 6
29 Australian Beg *H Southan*	3	59	52 10 0	50 0 0	50 0 0	55 0 0	55 1 0	54 18 0	55 10 0	50 0 0	52 0 0	53 13 6	54 17 6	..	..	56 0 0	10 0		168 0 0
	1610																		
EACH COMPANY'S PURCHASE			92	95	410		130	324	293	59			84	71		21			16994 5 0

Copper Ores FOR SALE SEPTEMBER 20, 1859.

	21 Cwts.
1 Cobre *Augusta Schneider*	32
2	3
3 *Acis*	85
4	12
5 *Stain's Castle*	105
6	104
7	91
8	64
9	63
10	61
11	59
12	54
13	10
14	9
15	6
16 *Hampshire*	166
17	86
18 Bearhaven.....	118
19	110
20	103
21	70
22 Parys.....	116
23	115
24 Knockmahon.....	8
25	56
26	49
27 Spanish ....*Farmouth*	85
28 Worthing Mine *Irene*	54
29 *Eclipse*	8
30 *Liberty*	14
31	8
32 Santander.....*Amitie*	70
33 Walwich Bay...*Athens*	57
34 Burnt Ores ...*Express*	57
35 Copper Slag ..*Liberty*	32
36	10
37 Namaqua *Cheshire Witch*	8
38 English and Canadian	2
39 Sundries.....	29
	2121

Pearse & Brown, Printers, Swansea.

Under the heading "Produces" there are, it will be noticed, two columns: in the first are stated the results of the assays, which have been made on behalf of the sellers, and about which no secrecy is maintained; the second is left blank, and is intended for the insertion of the results of the smelters' assays, which are kept rigidly secret. The sums immediately below which are the transverse lines in the columns of tenders are the highest bids, and, accordingly, those at which the ores were sold.

I now insert (see p. 305) a printed form of the results of one of the copper-ore sales at Truro, introducing only a few of the biddings by way of example, as the table is too long to be given in extenso.

Standard.—It will be remarked, that at the head of the last column but one on the right the term *standard* occurs; a term which is in common use, and is generally quite unintelligible to persons not actually engaged in copper-smelting. For the following history of its origin, and explanation of its present meaning, I am indebted to Mr. Keates, who designates it as an "everlasting stumbling-block of copper-trade technicality."

"Originally there were few copper-smelters and few miners, and it was customary for the former to contract with the latter to buy their ores for periods varying from a quarter to one year, agreeing to pay them for the same according to a *standard* price of copper determined on; and which price was usually the selling price of *tough-cake* copper at the time. Thus, if copper were selling at 120*l.* per ton, the *standard* was fixed at that rate, or thereabouts. Out of this *standard* price the miner returned to the smelter a certain sum on every ton of ore sold,[8] which for many years was fifty-five shillings per ton, though originally it was more. This was called the *returning charge*. The miner also gave the smelter 1 cwt. of ore upon every ton, to cover waste on removing the ore from the mine to the smelting-works: the smelter was also allowed a varying number of pounds of ore in each ton as compensation for moisture in the ore, the bulk being weighed *wet*, while the assayer's sample was weighed *dry*. *Examples.*—Suppose a bargain made, and the ore weighed by the miner to consist of two parcels, one of 1004 cwt., which is guessed to contain ½ cwt. of moisture per ton; the other of 800 cwt., which is guessed to contain ¾ cwt. of moisture per ton; so that in the first case the quantity of ore *paid for* is only 46 tons 14 cwt. 1 qr., and in the second it is only 36 tons 15 cwt. 2 qrs. Let the first parcel produce by assay 10½ per cent. and the second 5¼ per cent. of copper. In the first parcel the gross value of the copper in the ton of ore will be 12*l.* 12*s.*, the standard price of copper being 120*l.* For 100 parts of copper (say 1 ton) : 120*l.* :: 10½ parts : 12*l.* 12*s.* But from this gross value of the copper in the ton of ore the returning charge must be deducted. Thus, gross value of the copper 12*l.* 12*s.*; returning charge, 2*l.* 15*s.*; price per ton of ore, 9*l.* 17*s.* In like manner the price of the second parcel of ore will be found to be 3*l.* 11*s.* Thus far the term *standard* is simple and intelligible, meaning neither more nor less than the *price of copper*.

[8] The ton of copper ore is always 2352 lbs. or 21 cwts. if not otherwise expressed.

COPPER ORES SAMPLED OCTOBER 24, AND SOLD AT TABB'S HOTEL, REDRUTH, NOVEMBER 8, 1855.

MINES.	21 Cwts.	1. Mines Royal Co.	2. Vivian and Sons.	3. Freeman and Co.	4. P. Grenfell and Sons.	5. Williams' Crown Copper Co.	6. Sims, Willyams and Co.	7. Williams, Foster, and Co.	8. English and Australian Copper Co.	9. Mason and Elkington.	10. Frederick Bankart.	11. Copper Miners' Co.	Excess.	Amount of each Parcel.	Amount of each Mine.	Produce of each Parcel.	Standard of each Parcel.	Average Standard, Produce, and Price. Quantity of Ore, Copper, and Money, &c. &c.
		£. s. d.	£. s. d.	£. s. d.	£. s. d.	£. s. d.	£. s. d.	£. s. d.	£. s. d.	£. s. d.	£. s. d.	£. s. d.	s. d.	£. s. d.	£. s. d.			
WHEAL BULLER	165	5 4 0	6 2 0	6 7 6	6 6 6	6 2 0	6 4 6	6 4 6	6 9 0	6 6 0	5 15 6	6 0 0	1 6	999 15 0	. . .			Average Standard and Produce. £141 11 0 6¾.
	113	4 8 0	4 6 6	4 2 6	4 9 6	4 3 0	4 7 0	4 5 6	4 0 0	4 5 0	4 8 6	4 10 0	0 6	508 10 0	. . .			
	86	5 9 6	6 11 0	6 4 0	6 12 0	6 3 0	6 7 6	6 5 6	6 9 0	6 14 6	6 6 6	6 14 6	..	578 7 0	. . .			
	80	4 18 6	4 16 6	4 14 0	5 1 0	4 14 0	4 16 6	4 16 6	5 0 0	5 2 6	5 2 6	4 18 0	..	410 0 0	. . .			
	70	5 4 0	6 2 0	5 18 0	6 9 0	6 0 0	6 5 0	6 1 6	6 0 0	6 6 0	6 4 6	6 8 0	1 0	509 11 0	. . .			
	75	4 13 0	5 13 6	5 7 0	5 17 6	5 11 0	5 12 0	5 13 0	5 5 0	5 15 0	5 13 6	5 12 6	2 6	440 12 6	. . .			
	74	3 9 0	4 8 6	4 11 6	4 11 6	4 4 0	4 7 0	4 6 6	4 10 0	4 5 0	4 14 6	4 5 0	3 0	349 13 0	. . .			Average Price per 21 cwt. £6 15 6
	59	2 14 0	3 10 0	3 7 0	3 14 0	3 7 0	3 11 6	3 9 6	3 3 0	3 11 0	3 12 6	3 11 6	1 6	218 6 0	. . .			
	52	2 0 0	2 14 0	2 11 0	2 15 6	2 11 0	2 12 6	2 13 0	2 10 0	2 10 0	2 1 6	2 5 0	1 6	144 6 0	. . .			
811	38	6 10 0	7 11 0	7 17 0	7 18 0	7 10 0	7 8 0	7 12 6	7 16 6	7 10 0	7 8 6	7 12 0	1 0	300 4 0	4459 4 6			Quantity of Ore. 5013
	78	3 0 0	3 17 0	3 11 0	3 18 6	3 9 0	4 0 6	3 10 0	3 8 0	3 18 0	3 1 6	3 10 0	2 0	313 19 0	. . .			
WEST WHEAL BASSET ..... [*A portion of the detail of this and the following Mines is omitted to save space.*]	66	4 11 6	4 11 6	4 5 0	4 7 6	4 4 0	4 9 0	4 4 0	4 0 0	4 5 0	4 1 6	4 7 6	..	301 19 0	. . .			Quantity of Fine Copper. Tons. cwts. 336 9
	65	7 18 6	7 19 6	7 12 0	8 0 0	7 10 0	7 15 6	7 11 0	8 2 0	8 0 0	7 19 6	8 0 0	2 0	526 10 0	. . .			
	63	6 9 0	7 15 0	7 17 6	7 15 0	7 5 0	7 15 6	7 5 0	7 17 0	7 10 0	7 0 6	7 13 0	0 6	466 2 6	. . .			
	62	4 10 0	5 10 6	5 4 0	5 14 6	5 3 0	5 8 6	5 4 0	5 2 0	5 12 0	4 19 6	5 10 6	2 6	354 10 0	. . .			
606	26	7 17 6	8 3 0	8 5 6	8 5 0	7 12 0	6 7 0	7 13 0	7 17 0	8 0 0	8 0 6	8 3 6	2 0	215 3 0	3716 7 0			Amount of Money. £33,842 5 6
CARN BREA	526	....	....	....	....	....	....	....	....	....	....	....	..	....	3083 3 6			Amount of each Company's Purchase.
NORTH BASSET	416	....	....	....	....	....	....	....	....	....	....	....	..	....	2946 6 6			
PAR CONSOLS	370	....	....	....	....	....	....	....	....	....	....	....	..	....	3922 19 0			
ALFRED CONSOLS	279	....	....	....	....	....	....	....	....	....	....	....	..	....	2197 0 0			
HALAMANING	245	....	....	....	....	....	....	....	....	....	....	....	..	....	1617 9 0			
ROSEWARNE UNITED MINES	233	....	....	....	....	....	....	....	....	....	....	....	..	....	2541 12 0			
GREAT WHEAL ALFRED	180	....	....	....	....	....	....	....	....	....	....	....	..	....	877 3 6			
CLYJAH AND WESTWORTH	160	....	....	....	....	....	....	....	....	....	....	....	..	....	973 2 6			
LEVANT	150	....	....	....	....	....	....	....	....	....	....	....	..	....	915 1 6			
SOUTH CRENVER	134	....	....	....	....	....	....	....	....	....	....	....	..	....	418 19 6			
BOILING WELL	115	....	....	....	....	....	....	....	....	....	....	....	..	....	651 0 0			
WEST ALFRED CONSOLS	101	....	....	....	....	....	....	....	....	....	....	....	..	....	262 10 6			
WEST FOWEY CONSOLS	97	....	....	....	....	....	....	....	....	....	....	....	..	....	940 18 0			
TRELOWETH	79	....	....	....	....	....	....	....	....	....	....	....	..	....	320 12 0			
COOK'S KITCHEN	74	....	....	....	....	....	....	....	....	....	....	....	..	....	191 18 0			
BOTALLACK	71	....	....	....	....	....	....	....	....	....	....	....	..	....	619 6 0			
TRENOW CONSOLS	64	....	....	....	....	....	....	....	....	....	....	....	..	....	290 2 6			
WHEAL FRIENDSHIP	55	....	....	....	....	....	....	....	....	....	....	....	..	....	273 1 6			
WHEAL MARGERY	52	....	....	....	....	....	....	....	....	....	....	....	..	....	401 14 0			
WHEAL AGAR	34	....	....	....	....	....	....	....	....	....	....	....	..	....	199 8 0			
PROVIDENCE MINES	25	....	....	....	....	....	....	....	....	....	....	....	..	....	76 17 6			
WHEAL TREBARVAH	19	....	....	....	....	....	....	....	....	....	....	....	..	....	131 5 6			
BRITISH ARSENIC	18	....	....	....	....	....	....	....	....	....	....	....	..	....	7 10 0			
WHEAL TRENWITH	16	....	....	....	....	....	....	....	....	....	....	....	..	....	119 8 0			
WHEAL TREFUSIS	16	....	....	....	....	....	....	....	....	....	....	....	..	....	106 0 0			
CARBORNE CONSOLS	16	....	....	....	....	....	....	....	....	....	....	....	..	....	68 4 0			
EAST WHEAL VOR	12	....	....	....	....	....	....	....	....	....	....	....	..	....	35 2 0			
WHEAL HENDER	11	....	....	....	....	....	....	....	....	....	....	....	..	....	139 14 0			
GREAT WHEAL FORTUNE	10	....	....	....	....	....	....	....	....	....	....	....	..	....	180 3 6			
TRUTHALL	9	....	....	....	....	....	....	....	....	....	....	....	..	....	51 19 6			
WHEAL CUPID	9	....	....	....	....	....	....	....	....	....	....	....	..	....	64 2 6			
Each Company's Purchase	...	265 17½	847½	312	1216 17½	449½	466½	585½	406½	448½	321	361½						Standard and Produce of last Sale. £138 1 0. 7½.

Standard and Produce of corresponding Sale last Month. £142 19 0 7.

NO SALE ON THURSDAY, Nov. 15, 1855.

COPPER ORES For Sale on Thurs. Nov. 22, at the Royal Hotel, Truro.

MINES.

Devon Great Consols	1705
Phœnix Mines	641
West Carnbon	250
Hingston Downs	230
Wheal Arthur	170
Bedford United Mines	162
Wheal Friendship	159
Sortridge Consols	148
Collacombe	133
South Bedford	99
Wheal Zion	38
Balkwell's Ore	47
Hawk Moor	40
Wheal Langford	33
Wheal Crebor	25
Lady Bertha	22
Great Polgooth	15
Total 21 cwts	4028

PRINTED BY JAMES TREGASKIS, *At the Ticketing Paper Office*, REDRUTH.

SALE OF COPPER-ORES.

The sources of the smelter's profits were the care with which he got his ores transported from the mine to his works, so as to save as much as possible of the 1 cwt. of ore in each ton which he did not pay for, the portion of the 2*l.* 15*s.* returning charge which was not actually expended in smelting, and the *surplus*, or quantity of copper which his furnaces yielded in excess over the crucible of the assayer, and this of course would vary with the skill as well of the assayer as of the smelter. Originally copper-ores were dressed to a pretty uniform rate of produce, perhaps from 9 to 12 per cent., and, *whatever the produce*, the standard did not vary. By and by the ores were not dressed so uniformly; some came to market, say of 15 per cent. produce, others of 5 per cent. But the smelter, more acute than his neighbours, saw that he had better buy those of 5 per cent. and leave the others, because it took a much less portion of the 2*l.* 15*s.* to smelt a ton of ore of 5 per cent. than a ton of ore of 15 per cent. produce.[9] Now the simple mode of meeting this was to have had a varying scale of returning charges, instead of which these charges remained the same, while the standard was varied with the varying produce of the ores, so that with copper at 120*l.* there might be a standard of 115*l.* or 130*l.*, and thus the word standard lost its former simple and correct meaning. Competition went on increasing, processes were improved, carriage, freights, coals, &c., were lowered, but the *returning charge* continued the same, with, of course, less applicability than ever to the varying produce of the ores.

An illustration of what actually occurs at a modern sale will make the matter plain. Out of a modern sale of 3000 or 4000 tons of ore, varying in produce from 4 to 20 per cent., let us select the following lots, with the prices at which they were sold:—

			£.	*s.*	*d.*
100 tons of 5 per cent. produce		.....	4	12	0
id.	8	id.	8	1	0
id.	12	id.	12	18	0
id.	16	id.	17	8	0
id.	20	id.	21	15	0

The smelter has no longer got his *standard* price of copper arranged with the miner as of old, but he opens his eyes to all the circumstances, or ought to do; he sees what sort of ore he wants; he knows the rate of carriage and freight which he will have to incur on each parcel; he knows that one lot melts easily, another with difficulty, a third makes good copper, a fourth bad, and so on; and, in the end, he finds he has bought the five lots of ore above mentioned at the prices affixed. Immediately these *prices* are disclosed in the sale-room the miners' and smelters' clerks proceed to calculate *the standard* in the following manner:—

	£.	*s.*	*d.*
Price of the ore of 5 per cent. produce	4	12	0
Add returning charge	2	15	0
	7	7	0

But this sum refers to the *ton of ore*, or 5 per cent. of the *ton of copper*, so that the standard of the ton of copper will be 7*l.* 7*s.* × 20 = 147*l.*

[9] The father of the late Mr. Vivian, it is reported, was the first person clearly to apprehend this important commercial truth.

Again:—

	£.	s.	d.
Price of the ore of 20 per cent. produce	21	15	0
Add returning charge	2	15	0

This multiplied by 5 gives the standard of 122*l.* 10*s.* Hence *the standard is now deduced from the price, and not the price from the standard as formerly.* The buyer makes his offer without thinking of the standard. When the sale is over, the *average produce* of all the parcels of ore is determined, and also the *average standard.* Taking the 5 lots enumerated, the average produce is $12\frac{3}{16}$ nearly, and the average standard 132*l.* 4*s.* nearly. The only purpose which this modern standard serves is a ready mode of comparison of prices or of rates at which *copper in the ore* has been sold. For instance, instead of saying last week ores of 5 per cent. produce sold for such a sum and this week they sold for such a sum, the phrase is, the standard is down a couple of pounds, or up 5*l.*, as the case may be.

Copper-smelters in England and Wales.—I am indebted to Mr. Keates for the subjoined list of smelters in July, 1861.

Proprietors.	Name of Works.	Locality.
Pascoe Grenfell and Sons	Middle Bank	Swansea.
Do.	Upper Bank	Do.
Vivian and Sons	Hafod	Do.
Do.	Taibach	Aberavon.
Williams, Foster, and Co.	Morfa	Swansea.
Do.	Landore	Do.
Do.	Rose	Do.
Do.	Crown	Neath.
Sims, Willyams, and Co.	Llanelly	Llanelly.
Copper Miners' Company	Cwmavon	Aberavon.
Mona Mining Company	Mona	Amlwch.
Keys and Son	Whiston	Cheadle.
British and Foreign Company	Parr	St. Helen's, Liverpool.
Newton, Keates, and Co.		
Newton, Keates, and Co.	Sutton	Do.
Bibby, Sons, and Co.	Ravenhead	Do.
Mason and Elkington	Pembrey	Near Llanelly.
Charles Lambert	Port Tennant	Swansea.
Do.	Widnes Dock	Liverpool.
Frederick Bankart	Red Jacket	Neath.
Sweetland, Tuttle, and Co.	Britonferry	Do.
Vivian and Williams	White Rock	Swansea.
Williams and Vivians and others	Mines Royal[1]	Neath.
James Radley	Pocket Nook	St. Helen's, Liverpool.
Bold Copper Company	Bold	Do.

Associated copper-smelters.—There are certain of the smelting companies—about half—whose assayers act in concert, and assemble weekly, when each presents the results of his assays of the samples of ores announced for sale on a given day. The assayers compare their results and agree upon a uniform list of produces, which is called the

[1] Incorporated by Royal Charter, James I., A.D. 1564.

"settled list;" and by this the associated smelters are supposed to be guided in their biddings for the ores. But this may not always be the case. Thus, suppose the produce of a particular lot of ore to be returned as 9¼ per cent. by the private assayer of a company while it is only fixed at 9 per cent. in the "settled list," the company would probably bid on a produce of 9¼, and *vice versâ*. Admission to this conclave of assayers is believed to be of great advantage, because the error of any individual assayer is sure to be found out and corrected. The strictest secrecy is attempted to be maintained with respect to the "settled list," both the smelters and the assayers of the association in question being under a promise not to impart information concerning their proceedings to any "outsider." The companies have of course a perfect right to enter into a combination of this kind, but it is questionable whether it be wise on their part to affect so much mystery, and forbid the publication of the "settled list" *after* the sale. Secrecy engenders suspicion, and people are apt to conclude that deeds are kept in the dark because they will not bear the light. Thus many mine-adventurers are under the impression, which may be very erroneous, that all these strict injunctions as to privacy on the part of the associated smelters can have no other object than that of keeping down the price of ores. My own conviction is, that if the "settled list" were published in due course *after* the sale, all cause of suspicion would be removed, and the association would benefit rather than suffer. It has been reported that in making out the "settled list" only the *lowest* produces are selected, and that the average of *all the produces* is not taken; but, from what I have seen, I believe this report to be without sufficient foundation. Evidence on this subject will be presented under the head of Assaying in a subsequent part of this work. However, it is confidently asserted, that on one occasion good reason existed for disputing one of the produces set down in the "settled list." The following anecdote, which I received from an excellent authority, may be adduced in confirmation of this statement. Some years ago a rich copper-ore was assayed by a professional assayer of great experience, and reported by him to contain from 30 to 40 per cent. of copper. The produce, whatever it might be, was 5 per cent. higher than that in the "settled list." On the ticketing-day the particular lot of ore was presented for sale, when, on account of the discordance above mentioned, and which came to be known, a proposal was made to withdraw it. Some of the smelters present objected to this proposal on the ground that it was not likely that the assays of their united assayers should all be wrong and the assay of a single assayer correct. At this period the manager of certain copper-works rose, and with a degree of moral courage which did him honour, boldly avowed that his private assay was 4½ per cent. higher than that of the settled list. This decided the point, and its sale was postponed. It was subsequently sold at a price corresponding to the higher produce of the single assayer. I have recorded this anecdote simply to show that the "settled list" may not, in every case, be quite infallible.

Ores of Copper.

Under this head an enumeration of the various mineral species which are subjected to metallurgical treatment will be given, and their composition stated; but for information respecting their physical characters the reader is referred to any of the excellent standard works on Mineralogy.[1]

1. *Native copper.*—It is not an unfrequent constituent of certain copper-ores. It occurs diffused in isolated particles, in the form of thin laminæ, in dendritic pieces, and in solid blocks, occasionally of large dimensions. On breaking pieces of ore, a nucleus of metallic copper may sometimes be found, coated successively with red oxide and carbonate of copper. The richest deposits of native copper which have been discovered are those of Lake Superior, in North America. My friend Professor Brush, of Yale College, U.S., has communicated to me the fact that in 1858 6000 tons of copper were procured from the native copper of Lake Superior alone. Mr. Petherick, the well-known mining engineer, informs me that at Minnesota in 1854 not fewer than forty men were engaged during twelve months in cutting up a single mass of native copper weighing about 500 tons! Native copper is generally believed to be extremely pure; but I do not find that many analytical examinations of it have been made. That it is not necessarily pure, is shown by the analysis recorded at p. 286. The native copper at Lake Superior in some places occurs curiously intermingled, but generally not alloyed with, native silver. Hautefeuille analysed a specimen from this locality which contained both silver and mercury. The results of his analysis are as follow[2]:—

Copper 69·280, Silver 5·453, Mercury 0·019, Matrix 25·248.

A considerable quantity of ore is imported into Swansea from Chili under the name of "copper sand" or "copper barilla;" it consists of from 60 to 85 per cent. of metallic copper intermixed with quartz.

Native copper is generally remarkable for its toughness. Mr. Morgan, of the Hafod Works, informed me that the toughest copper he had ever seen was a piece of native copper from Chili, about three-eighths of an inch in thickness: it was bent backwards and forwards forty-eight times before breaking.

2. *Red oxide of copper*, Cu^2O.—When pure it contains 88·78 per cent. of copper. It occurs in Cornish, South American, and especially Australian ores.

3. *Black oxide of copper*, CuO.—When pure, it contains 79·82 per cent. of copper. As obtained from the mines it is frequently very impure. It occurs at Lake Superior.

4. *Green carbonate of copper, or malachite*, $CuO, CO^2 + CuO, HO$.—When pure it contains 57·33 per cent. of copper. It is a frequent consti-

[1] Amongst these may be mentioned the following:—Phillips's Mineralogy, by Brooke and W. H. Miller, 8vo, Longman and Co., London, 1852; A System of Mineralogy, by James D. Dana, 2 vols. 8vo., New York and London, 1854; Elemente der Mineralogie, von Dr. C. F. Naumann, 8vo. Leipzig, 1846.

[2] Uebersicht, Kenngott, 1860, p. 108.

tuent of copper-ores. It has been largely imported from South Australia. In analyses of this mineral from various localities, no other constituents are recorded than oxide of copper, carbonic acid, and water.

5. *Blue carbonate of copper*, $2\,CuO, CO^2 + CuO, HO$.—When pure it contains 55·16 per cent. of copper. A considerable quantity of this mineral was formerly obtained at Chessy, near Lyons, in France. It has been imported from South Australia in admixture with green carbonate. From the analyses of this mineral which have been published, it would appear to be equally free from foreign matter as the green carbonate. It must, however, be borne in mind that mineralogists would only select for analysis specimens of the greatest purity. Although the mineral species themselves may be pure, yet they may occur in association with other substances, which would cause them to yield an inferior quality of copper. Thus I was assured that the carbonate ores from Kanmantoo, in Australia, contained antimony and bismuth. Generally the copper produced in the smelting carbonates is of the best quality.

6. *Vitreous, or grey sulphide of copper*, Cu^2S.—When pure it contains 79·79 per cent., or nearly four-fifths of its weight, of copper. It is of frequent occurrence in Cornwall. In nine analyses of this mineral recorded by Rammelsberg,[3] iron appears as a constituent, varying in amount from 0·5 to 3·33 per cent.

7. *Purple copper*, $3\,Cu^2S + F^2S^3$.—When pure it contains 55·54 per cent. of copper. It generally occurs massive and disseminated, and but very seldom crystallized. Rammelsberg has classified the varieties of purple copper according to the proportion of copper which they contain: in the 1st class, the copper ranges from 56 to 58 per cent.; in the 2nd, from 60 to 64 per cent.; and in the 3rd, it is fixed at 70 per cent. The following selected analyses furnish examples of each of these classes[4]:—

	1st Class.		2nd Class.		3rd Class.	
	1.	2.	3.	4.	5.	6.
Copper	56·76	56·10	60·80	61·07	69·72	70·0
Iron	11·84	17·36	13·67	14·00	7·54	7·0
Sulphur	28·24	25·80	25 46	23·75	22·65	22·3
	99·84	99·26	99·93	98·82	99·91	99·3

No. 1. From the Condurrow mine, Camborne in Cornwall, by Plattner. No. 2. From Sweden, by Plattner. No. 3. From Coquimbo, Chili, by Böcking. No. 4. From Killarney, Ireland, by Phillips. No. 5. From Eisleben, Prussia, by Plattner. No. 6.—From Tuscany, by Berthier. The *rational* constitution of some of these minerals at least has not been satisfactorily established.

8. *Copper-pyrites, or yellow copper-ore*, $Cu^2S + Fe^2S$, or, as it was for

[3] Handbuch der Mineralchemie, 1860, p. 50.

[4] Op. cit., p. 113.

merly expressed, CuS + FeS.—When pure, it contains 34·81 per cent. of copper. It is the most abundant ore of copper. It is largely imported from Cornwall, Devonshire, Cuba, and South America. Magnificent specimens of it are yielded by a rich mine in Tuscany. In eight analyses of this mineral recorded by Rammelsberg, no mention is made of the presence of any foreign matter, except a little quartz. In the ore raised at the Fowey Consols Mines in Cornwall, and in which the copper exists in the state of copper-pyrites, both nickel and silver occur in small quantity; but whether they actually exist in the copper-pyrites itself I am not aware. In ores containing this mineral iron-pyrites is frequently present in large quantity.

9. *True grey-copper ore, or fahlerz.*—This ore is found in numerous localities, and is very complex and variable in composition. It may be divided into three principal classes, of which the following analyses are selected as examples[5]:—

1. Antimonial Grey-Copper Ore.

	1.	2.	3.	4.
Copper	30·47	34·48	37·11	37·95
Antimony	26·56	28·24	25·97	28·78
Silver	10·48	4·97	1·09	0·67
Iron	3·52	2·27	4·42	2·24
Zinc	3·39	5·55	5·02	2·52
Lead	0·78	..	0·54	..
Sulphur	24·80	24·73	23·76	25·82
	100·00	100·24	97·91	97·98

No. 1. From Neudorf, Harz, by Rammelsberg. No. 2. From Clausthal, by H. Rose. No. 3. From Durango, Mexico, by C. Bromeis; 0·47 of matter was left undecomposed. No. 4. From Goslar, Harz, by Rammelsberg.

2. Arsenical Grey-Copper Ore.

	1.	2.	3.	4.
Copper	47·70	51·62	41·07	42·60
Arsenic	12·46	19·03	18·87	19·01
Iron	9·75	1·95	2·22	9·21
Zinc	..	..	8 89	..
Lead	..	..	0·34	..
Sulphur	30·25	26·61	28·11	29·18
	100·16	99·21	99·50	100·00

No. 1. Tennantite, from the Trezavean mine, Redruth, Cornwall, by Phillips. No. 2. Tennantite, from the same locality, Rammelsberg. No. 3. From the Prophet Jonas mine, Freiberg, by Plattner. No. 4. Modum, Norway, by Fearnley.

[5] Rammelsberg, op. cit., p. 86 et seq.

3. Grey-Copper Ore containing both Antimony and Arsenic.

	1.	2.	3.	4.	5.	6.
Copper	38·42	37·98	39·18	40·57	38·63	30·73
Antimony	25·27	23·94	23·66	21·47	16·52	17·76
Arsenic	2·26	2·88	4·40	2·42	7·21	11·55
Silver	0·83	0·62	..	0·56	2·37	10·53
Iron	1·52	0·86	6·99	2·92	4·89	1·42
Zinc	6·85	7·29	..	5·07	2·76	2·53
Sulphur	25·03	25·77	25·64	26·10	26·33	25·48
	100·18	99·34	99·87	99·11	98·71	100·00

No. 1. From the Aurora mine, Dillenburg, by H. Rose: this mineral gave a red streak. No. 2. From Kapnik, Hungary, by H. Rose; streak red. No. 3. From Cornwall, by Wittstein. No. 4. From Beresow, Siberia, by Löwe; the 0·56 of silver was inclusive of some vein-stuff. No. 5. From Gersdorf, Freiberg, by H. Rose; streak black. No. 6. From North Carolina, U.S., by Genth; streak brown-red.

Grey-copper ores containing mercury has been found in Hungary, the Tyrol, and Tuscany.[6] In eleven analyses recorded by Rammelsberg, the mercury ranged from 0·52 to 17·27 per cent. Much has been written on the subject of the rational constitution of grey-copper ores, and numerous and complicated formulæ have been proposed; but not until we know more concerning the so-called foreign matter, or, as some mineralogists designate it, "dirt," is it probable that satisfactory formulæ will be established.

10. *Chrysocolla.*—It is essentially a hydrated silicate of protoxide of copper. Two species are accepted of the formulæ $3\,CuO, 2\,SiO^3 + 6\,HO$ and $2\,CuO, SiO^3 + 3\,HO$.[7] Both, I presume, are confounded under the general term of Chrysocolla. The following analyses will suffice for illustration.

	1.		2.
Silica	32·55		40·09
Protoxide of copper	42·32		27·97
Sesquioxide of iron	1·63	Protoxide of iron	4·94
Lime	1·76		1·49
Magnesia	1·06		0·78
Water	20·68		24·73
	100·00		100·00

No. 1. From Lake Superior, by Rammelsberg. No. 2. From Chili, by Kittredge.

11. *Atacamite.*—It is esentially a hydrated oxychloride of copper, of the formula $CuCl + 3\,CuO$, combined with different proportions of water. It occurs in Chili, and other parts of the West Coast of South America. The following analyses of crystallized mineral from Copiapó were made by Field:—

	1.	2.
Chlorine	11·94	15·01
Protoxide of copper	70·74	70·48
Water	17·79	18·00

[6] Rammelsberg, op. cit., p. 89.

[7] Ibid., op. cit., p. 551.

These results lead to the formula $2(CuCl+3CuO)+9HO$. A considerable quantity of this interesting mineral has been imported into Swansea, where I have seen it in the ore-yards.

I am indebted to my valued friend and colleague, Mr. Warington W. Smyth, Lecturer on Mining at the Government School of Mines, for the following notice of the copper-mines of Devon and Cornwall. Mr. Smyth's position as Mining Inspector on behalf of the Duchy of Cornwall gives him peculiar facilities for obtaining accurate information on this subject.

Copper-ores of Cornwall and Devon.—Although a certain character may distinguish the ores of particular mines, it is subject to vary with the different depths at which productive courses of ore may occur; and at most of the mines considerable discrepancy will be found among the various "parcels," according to their being produced from various lodes within the same sett, or at various depths from the surface.

Among the most persistent characters may be cited the association of the copper glance (disulphide of copper) in the mines of the St. Just and St. Ives district (Botallack, Levant, Pendean, St. Ives Consols) with hæmatitic iron-ores, occasionally crystallized as specular iron, with jasper, and more rarely with bismuth, &c. The same mixture of sesquioxide of iron with this rich ore of copper is very noticeable again in the valuable group of mines (equally important for tin) which lie on the flanks of the granite between Camborne and Redruth, Dolcoath, Tincroft, Cook's Kitchen, and Carn Brea. From some of the lodes producing the copper-glance, copper-pyrites is altogether absent; in some cases the latter ore occurs at greater depth than the former. Sometimes at the same depth one lode will contain only the one ore, a neighbouring vein only the other, as in the neighbour lodes of Botallack Crowns lode and Wheal Cock lode, of the old Levant lode and the North lode.

Iron-pyrites and quartz are the most abundant concomitants of the copper-ores generally, the former especially so in some of the coarse and often large lodes, the character of which can often be inferred from the price obtained at the ticketings.

Carbonate of lime is rare, and generally confined to crystals lining a few drusy cavities: the same may be said of barytes, hitherto found only in the United Mines and a few mines in the Liskeard district.

Chlorite (*peach*) is a constituent of most of the lodes in one part or other; but in some instances, as in the Par Consols district, appears in great abundance, and very commonly as the accompaniment of a copper-pyrites of unusually rich colour and high per centage.

With the chlorite, as well as with some of the previously cited associates of copper ore, tin-stone very often occurs, and sometimes so mingled with the copper-ores, both pyrites and sulphide, as to render the separation by picking and dressing very difficult.

Fluor-spar is an important constituent of the matrix in several of the groups of mines, especially some of those placed in or very near the granite, as in the South Frances, Bassett and Buller group, Kelly Bray, Gunnislake and Bedford United, &c.

Carbonate of iron is a frequent companion of copper-pyrites. It may be specially noticed in the Devon Consols and Tavistock group of mines, and in a variety of crystalline forms at Fowey Consols. Among the rarer accompaniments may be mentioned wolfram, isolated crystalline portions of which may be seen in the ores of St. Day, United, Holmbush, Hingston Down, and Gunnislake.

Galena and zinc-blende, although not of unfrequent occurrence in moderate quantity in the copper lodes, are not very characteristic of the ores sold from particular mines.

The grouping of the ores is often remarkably similar in lodes placed under the same conditions, as an example of which we may take a beautiful association of rich and finely-coloured ores in the lodes of Phœnix and of South Frances, both working at considerable depth in granite, and yielding in some parts good copper-pyrites; in others, and the more gossany portions—malachite, chrysocolla, cuprite, and the delicate crimson tufts of chalcotrichite—which relieve the green and blue tints of the former species.

The Welsh Process of Copper-smelting.

This method consists of not less, and generally more, than six distinct operations. Reverberatory furnaces are exclusively employed; and of these there are only two kinds—calciners and melting furnaces. The fuel consists of a mixture of binding and free-burning coal, which is burned on a bed of clinker in the manner previously described. The process is varied somewhat in different establishments; but the modifications are not considerable. I shall first describe the process, as it may be conducted with the smallest number of operations, and as I saw it practised in 1848 at the Hafod Works, near Swansea. I have much pleasure in publicly acknowledging my obligation to the late Mr. Vivian for granting me free access to these works; and to Mr. William Morgan, the Manager, for much valuable information which, with the consent of Mr. Vivian, he so willingly afforded me.

Furnaces employed.—*Calciner.*—I am indebted to a firm near Swansea for the drawings from which the annexed engravings are taken. Some

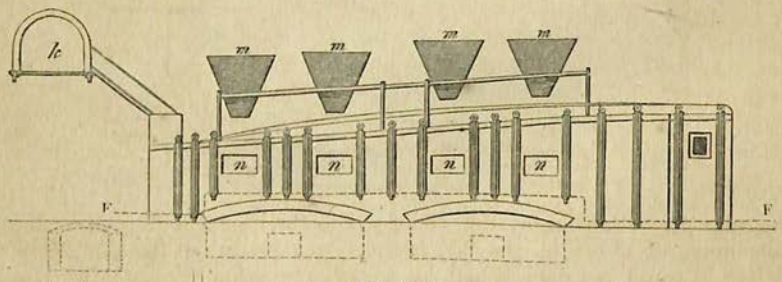


Fig. 77. Side elevation.

details of minor importance have been suppressed; and in the vertical sections the parts in view beyond the lines of section are not indicated.

But all the details which furnace builders usually consider necessary are represented. The interior of the furnace, which is exposed to the highest temperature, is built of fire-brick, while the exterior and parts under the bed are built of common brick. The fire-place is at one end; *a* is the ash-pit, above which are three transverse wrought-iron bars, as shown in section, fig. 78: on the two uppermost the bars of

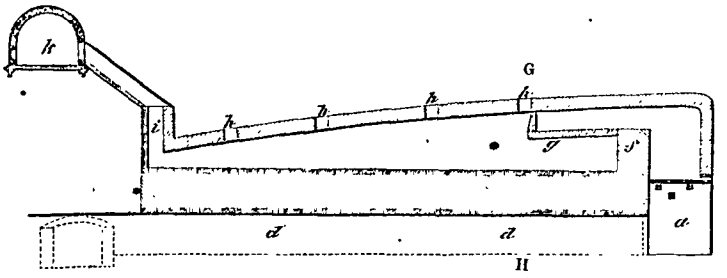


Fig. 78 Vertical section on the line A B, fig. 81 (see p. 316).

the grate rest, and the lower one serves as a support for the long crowbar employed in "breaking the grate;" *f*, the fire-bridge; *g*, an arch extending across the furnace from one side to the other, and intended to protect the ore on the bed underneath nearest the fire-bridge from exposure to too high a temperature. There are four rectangular openings, *h*, *h*, &c. in the roof, through which the ore is allowed to fall into the furnace from the hoppers or bins, *m*, *m*, &c., supported by a framework of wrought iron; each opening is closed by placing a large fire-brick over it. Each hopper may be made of four cast-iron plates tapering downwards, and firmly braced together. The bed is flat; on each side are square openings, *i*, *i*, &c., through which the ore after calcination is transferred to chambers or vaults underneath; during the process of calcination these openings are kept covered with fire-bricks. There are four doors *n*, *n*, &c.; on each side of the furnace in front of the openings *i*, *i*, &c., respectively. In fig. 79 are shown tri-

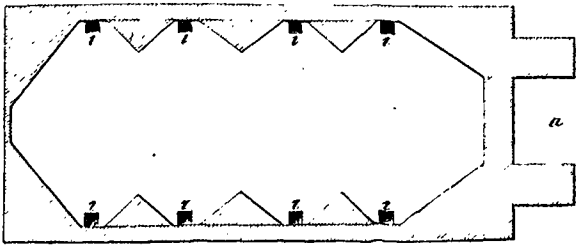


Fig. 79. Horizontal section, showing plan of the bed.

angular projections of brick-work, of which the object is to prevent the accumulation of ore on the bed of the furnace between the side doors, where it could not be reached by a rake, or "rabble," except at great inconvenience from the opposite side. At the end opposite the fire-place is a flue *i*, communicating with a large flue *k*, which is supported on iron plates and communicates with a high stack: several furnaces

are connected with the flue *k*. Below the bed are four arched brick-chambers, *b*, *b*, &c.; which, above, communicate with the openings *i*, *i*, &c., by the channels *l*, *l*, as shown in fig. 82; and, below, with the horizontal flues *d*, *d*, &c. by means of the openings *c*, *c*, &c. These flues are connected with a large flue, *e*, *e*, leading into the stack: by this arrangement any sulphureous vapour which may continue to escape from the ore, after it has been allowed to fall into the chambers *b*, *b*, &c., passes into the flue *e*, *e*, and is thereby prevented from incommoding the workmen. Fig. 80 shows the manner of placing the

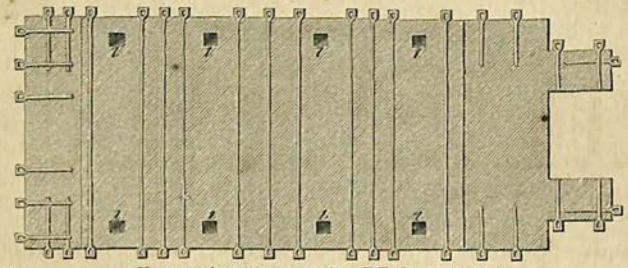


Fig. 80. Horizontal section on the line E F, fig. 77 (p. 314).

wrought-iron cramps, into which fit the lower ends of the cast-iron standards (see fig. 77); the upper ends of these standards are connected

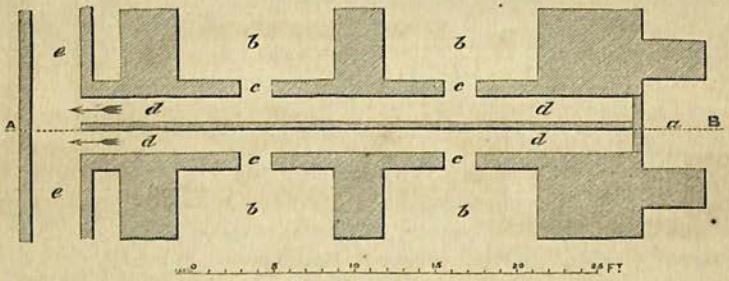


Fig. 81. Plan of foundation.

by wrought-iron tie-bars extending above the roof of the furnace, from side to side and from end to end. Some of the cramps pass quite

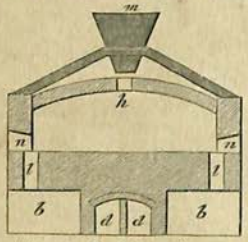


Fig. 82. Vertical section on the line G H, fig. 78.

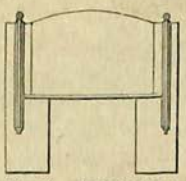


Fig. 83. End elevation of the fire-place.

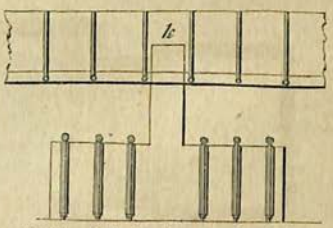


Fig. 84. End elevation near the stack.

through the furnace, and others which are short only a little way into the brick-work: the latter should be curved at the ends, directed inwards. Each opening *n*, *n*, &c., is formed of a cast-iron door frame,

having a sheet-iron door fixed on hinges at the top, so that it may open outwards and upwards. The clinker grate is used in this furnace. This calciner is much larger than usual, and is charged with about seven tons of ore at a time.

The annexed engravings represent a calciner of ordinary dimensions, and, I believe, of the best construction. The drawings of this furnace

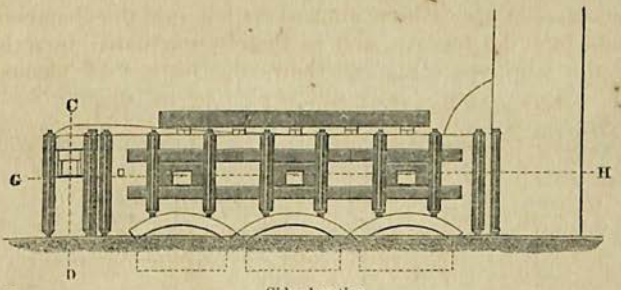


Fig. 85. Side elevation.

were kindly prepared by Mr. John Keates, expressly for this work. The description of the large calciner which has just been given will

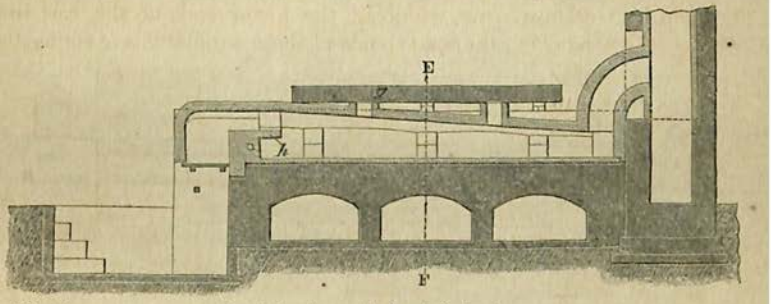


Fig. 86. Vertical section on the line A B, fig. 87.

in great measure apply to this, so that only a short additional explanation is necessary. There is a channel *o*, *o*, extending across the furnace

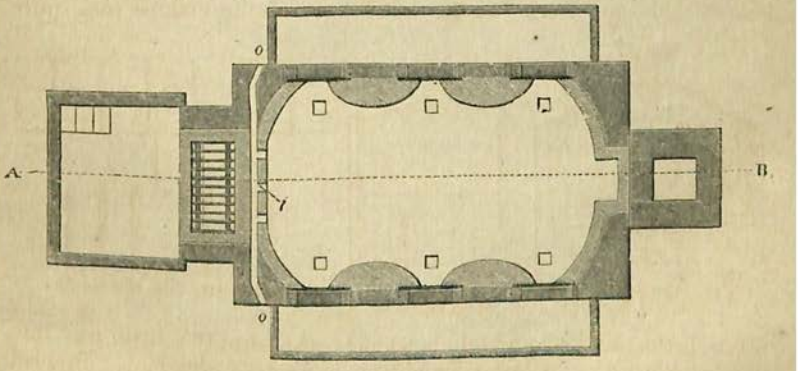


Fig. 87. Horizontal section on the line G H, fig. 85.

through the fire-bridge and open at each end; from this channel proceed three passages, *i*, through which the external air may enter the furnace. Above these passages is the "curtain-arch," *h*, of which the object has been stated in the description of the large calciner. By this construction, which was patented in 1812 by William Evetts Sheffield,[8] the fire-bridge is not only cooled, but air is admitted where it is required in the process of calcination. The bosses, or projections of brick-work, between the side-doors are rounded, and not triangular. There are two openings in the roof, which communicate with one large hopper, or bin, *g*. The light sectional shading of the internal brick-

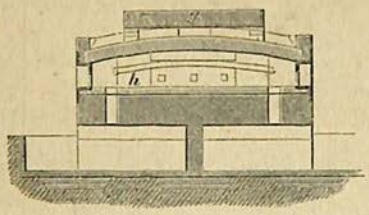


Fig. 88. Vertical section on the line E F, fig. 86.

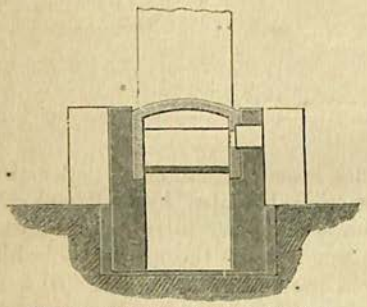


Fig. 89. Vertical section on the line C D, fig. 85.

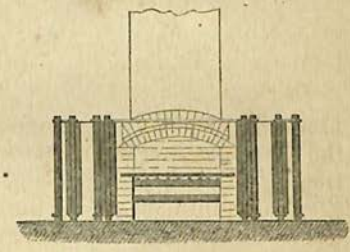


Fig. 90. End elevation of fire-place.

work represents fire-brick. The mode of bracing the furnace together is clearly shown in figs. 77 and 78. This calciner is charged with about three tons of ore at a time.

Melting furnace.—For the drawings from which the annexed engravings were made, I am indebted to the same firm who supplied me with those of the large calciner: *a*, *a*, side-walls of the fire-place; *b*, *b*, walls, which are carried up vertically, and enclosed above by the arch *o*; an arched chamber, *n*, is thus formed, which extends from the back of the ash-pit, *m*, to the opposite end of the furnace, where it is closed by a vertical wall. Upon the top of the arch is a flat platform of brick-work, *g*, *g*, fig. 93, upon which the bed of the furnace is built, and which has the form shown by the white space, *g g*; it is surrounded by vertical walls up to the springing of the arched roof, *p*, which forms the top of the furnace, and extends from the fire-place to the stack: a large, more or less oval-shaped, chamber is thus formed, which is filled to a considerable depth with sand, of which analyses have been previously given, see *q*, fig. 92. The upper surface of the sand is shaped into a shallow cavity, which gradually inclines from all sides towards the bottom of the tap-hole, *h*, through which the

[8] Specification 3612, A.D. 1812. Printed 1856.

metal is allowed to flow from the furnace. The fire-place, *d*, is, it will be observed, very large compared with that of a calciner. In the

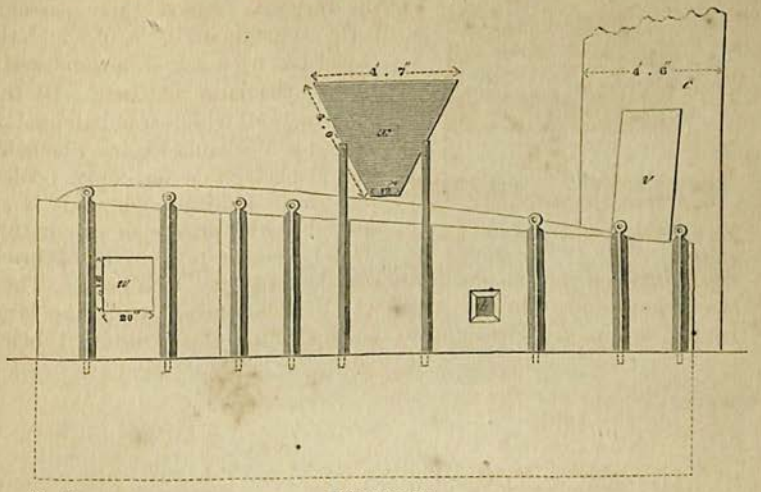


Fig. 91. Side elevation.

fire-bridge is left a narrow rectangular space, which, below, opens into the ash-pit, *m* ; on the right this space is bounded by a plate of cast-iron, *f*, called the bridge-plate, which is necessary to support the wall, *e*. Coal is introduced into the fire-place through the opening, *w*, which has no door, and is kept more or less perfectly closed with coal. An opening, *l*, is left above the bars, as is usual in reverberatory furnaces. The front wall of the fire-place rests on a cast-iron bearer, as shown

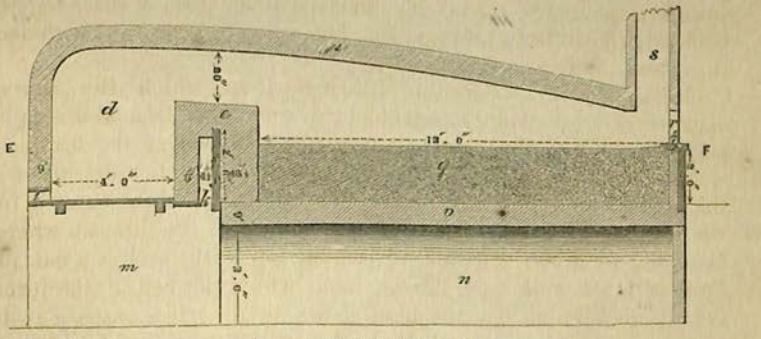


Fig. 92. Vertical section on the line A B.

above *l*, and the back wall rests on a similar bearer, *k*. In the roof there is a square hole, immediately above which is the iron hopper, *x*. The furnace is charged with ore through this hole, of which the size and position may be found from figs. 91 and 97 ; but the pieces of slag which form part of the charge are introduced through the end opening. The bottom of the hopper may be closed or opened by means of a sliding plate, which is fitted therein. At the end of the furnace

near the stack is an opening, *r*, through which the contents may be rabbled, and the slag drawn out. The sides and top of the opening are formed of large fire-bricks; but the bottom is formed by a cast-iron

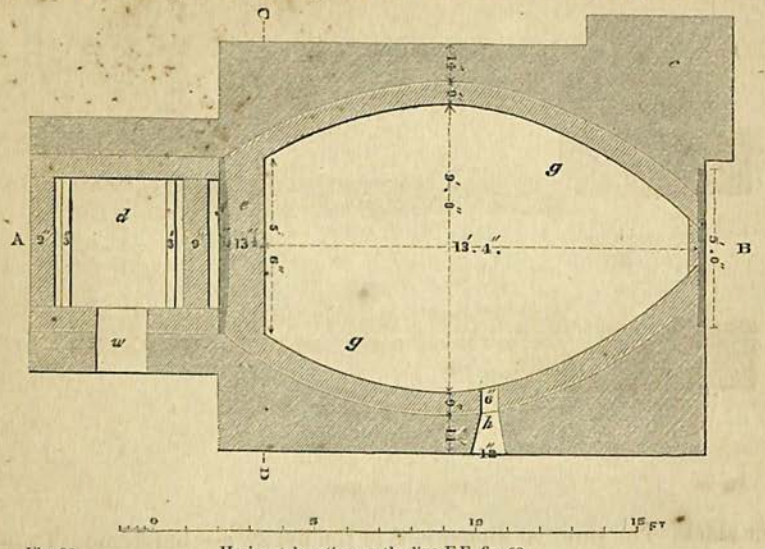


Fig. 93. Horizontal section on the line E F, fig. 92.

plate, *t*, below which is a vertical cast-iron plate, *i*; the outer edge of the plate, *t*, projects slightly; these plates are desirable in order to facilitate the removal of the slags and protect the bricks. The opening

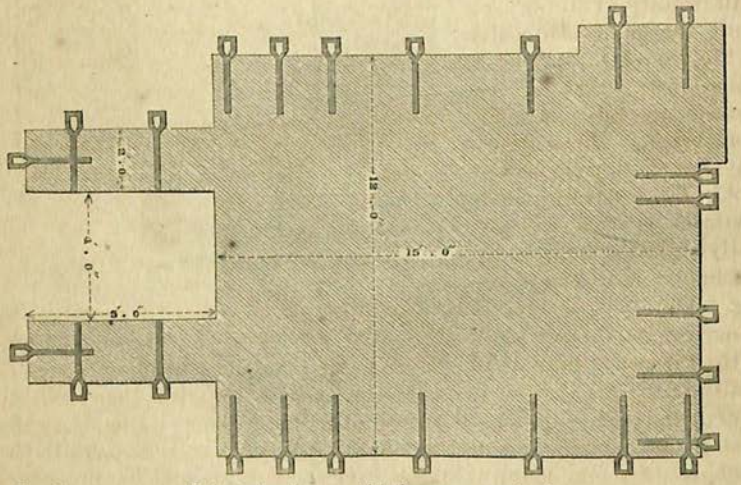


Fig. 94. Horizontal section on which the cramps are placed.

is closed with a large fire-brick, or quarry, in which is a small hole to enable the furnace-man to see the interior of the furnace, and form a judgment concerning the temperature. There is also a similar peep-

hole in the flue leading to the stack. Immediately above the opening, r, is the flue, v, connecting the furnace with the stack, c. Each furnace may have a separate stack, or many furnaces may be connected with

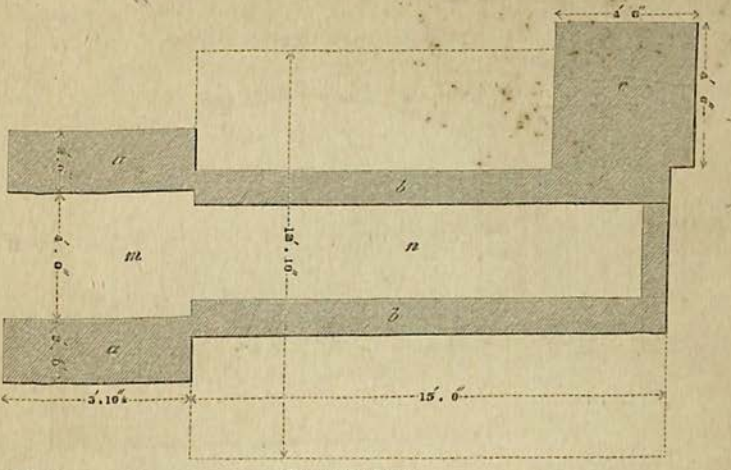


Fig. 95. Plan of foundation.

one stack. The internal dimensions of the flue, v, are important. They must vary according to circumstances, especially the height of the stack and the quality of the fuel. The inner-walls of the fire-place and body, the roof, and the interior of the stack are built wholly of fire-brick; while the outer side-walls of the fire-place and outer walls of the rest of the furnace are built of common brick. Dinas brick may be employed in the roof. The parts in which fire-brick is used are specially indicated in fig. 93 by the lighter sectional shading.

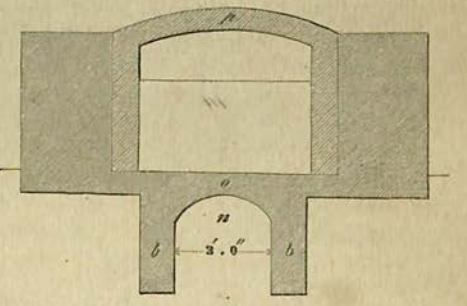


Fig. 96. Vertical section on the line C D, Fig. 93.

The stack is braced by vertical rods of iron tied together by transverse rods of iron passing through the brick-work. The sand bottom of the furnace is prepared in the following manner: Sand, to the depth of about a foot, is first put in and well pressed down; it is then strongly heated, and some *metal-slag* is spread over the surface and melted: the sand is thus more or less consolidated. A second layer of sand to the thickness of a few inches is spread over the surface, and the process of heating with slag repeated; and even a third layer may be added and set in a similar manner. The total thickness of the sand bottom may be about 20 inches; but in the furnaces of some works it is only about 12 inches thick, and consists of one layer. The presence of the

small amount of lime in this sand may be important, and act in the same way as lime in the manufacture of Dinas bricks, namely, by

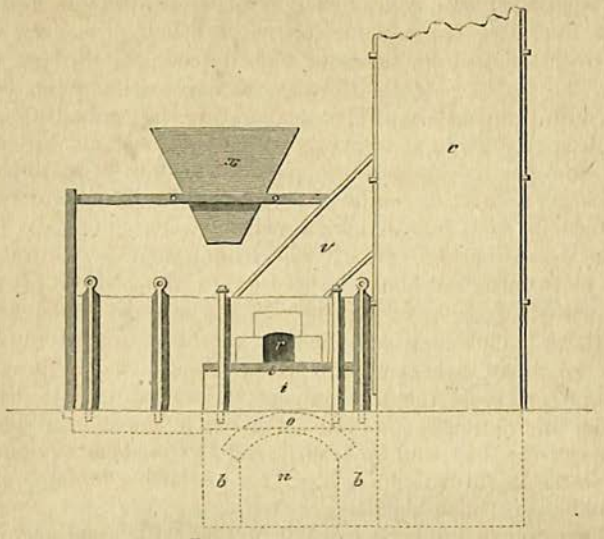


Fig. 97. End elevation near the stack.

tending to solder the particles together by the formation of silicate of lime, and so rendering the bottom solid and less pervious than it otherwise would be. In the *metal* and *refining* furnaces the sand bottom always consists of two layers, the lower one 9 inches thick and the upper one from 3 to 4 inches thick. It is only the upper one that is renewed at intervals, the lower one being seldom disturbed.

Copper-smelting in six operations.—For the sake of brevity and facility of reference, I shall distinguish these operations by the numerals from 1 to 6 respectively. It is only when there is a plentiful supply of carbonates of copper that the number of operations can be reduced to six. Ores of different kinds and from different localities are generally mixed, so that the mixture may on an average contain from 8 to 10 per cent. of copper.

Copper-smelting at the Hafod Works in 1848, *to which the first description applies.*—The mixture of ores consisted of the following varieties: *Yellow ore*, Fowey Consols Mine, Cornwall; copper and iron pyrites, Wheal Friendship, Devonshire; *Cobre ore*, Cuba, copper-pyrites, containing about 28½ per cent. of copper; *Cobre dust*, Cuba, copper-pyrites, containing about 12 per cent. of copper; cupriferous residues of oxide of iron produced by the calcination at sulphuric acid works of iron-pyrites containing copper from Ireland, known as *Irish ore*; *vitreous-copper* in admixture with iron-pyrites and hæmatite from the Levant Mine, Cornwall; residues rich in oxide of iron obtained in the calcination of cupriferous tin-ores in Cornwall, known as *burnt leavings*; and *red oxide* of copper with *blue* and *green carbonate*, Burra-Burra, Australia.

1. This operation is essentially a process of roasting; but it is

technically termed *calcination*, to distinguish it from a subsequent operation to which the term roasting is specially restricted. The *calciner* is charged with from 3 to 3½ tons of ore, through two holes in the roof, from two hoppers, one above each hole. The ore is spread evenly over the bed by means of tools introduced through the side-doors. The interior of the furnace is necessarily much cooled by contact with the cold ore. The temperature is gradually raised, and the ore is stirred about at intervals with long iron tools, called stirring rabbles, in order to expose every part in succession to the action of the gaseous products of combustion and the air, which enters through the side-doors, and, in calciners constructed on Sheffield's principle, through the fire-bridge also. The calcination is continued from twelve to twenty-four hours, according to the nature of the ores. At no period of the operation should the heat be sufficient to cause the particles to clot, or sinter together, as the action of the air upon clotted ore must, necessarily, be very imperfect. In proportion as calcination proceeds, the tendency of the ore to clot is diminished. When the calcination is completed, the ore is raked into the holes on the sides of the bed, and so transferred to the chambers underneath, where water is thrown upon it. The prevailing colour of the ore when cold is brownish black.

2. The calcined ore from No. 1 is melted with *metal slag*, a product subsequently obtained in operation No. 4, in a melting furnace termed the *ore-furnace*. The products are a regulus, termed *coarse-metal*, containing about 35 per cent. of copper, and *ore-furnace* slag, which is thrown away. The tap-hole in the side having been stopped with a mixture of clay and sand, the ore is let down into the furnace through the hole in the roof from the hopper above, to which it is carried in boxes containing 1 cwt. each. It is then spread evenly over the bottom, and slag is thrown in through the opening near the stack, after which both openings are closed and the fire made up. When the charge is melted, as it should be in about 5 hours, the fused mass, consisting of regulus and slag, is well rabbled, after which the slag is skimmed off and drawn out through the end opening. The furnace is again charged in a similar manner with calcined ore and slag, and the operation conducted as above described. When the bed of the furnace has become filled with melted regulus, or *coarse-metal*, the tap-hole in the side is opened and the regulus is granulated by causing it to flow in a small stream into a pit filled with water in close proximity to the furnace. The pit is lined with brick, and is usually about 4 feet square and 8 feet deep; at the bottom is a shallow open box, which is perforated at the bottom with numerous small holes, and may be raised either by a crane or pulley-blocks attached to a common tripod formed of poles. The granulated regulus, or *coarse-metal*, may thus be conveniently raised and drained. I have occasionally heard loud and repeated explosions produced by this process of granulation, which, I presume, are to be referred to the action of water in the spheroidal state. This result occurs when the metal is allowed to flow too rapidly into the water. It is very important that the slag should

have the proper degree of consistency. If too thin, there is always greater loss of copper, because the separation between the regulus and slag is not so apparent to the workman as when the slag is stiffer, and it becomes, consequently, more difficult to skim it off without at the same time drawing out some of the regulus. On the surface of the water in the granulation pits a yellow scum collects, resembling sulphur in appearance, and a bath of this water is in request as a cure for mangy dogs. It is said to be poisonous, and, therefore, probably contains arsenic.

The slag is received into long, narrow, shallow, more or less rectangular, parallel cavities in sand, termed sand-moulds or beds, in front of, and below, the end opening of the furnace. These cavities are connected together by gutters in the middle and upper part of the partition walls of sand which separate them from each other. The slag after filling one cavity overflows into the next, and when this is full it passes into the third, and so on in succession. The regulus which may be accidentally drawn out of the furnace collects chiefly at the bottom of the cavity into which the slag first flows. When the slag is cold, it should be broken in pieces and examined before it is thrown away, and any which may be found to contain any sensible amount of regulus must be put aside to be remelted. When a piece of cold slag is freshly broken, very small shots of regulus may easily be detected on the fractured surface by their lustre and the difference of colour between them and the slag in which they are imbedded. I have examined many of the slag-tips of copper-works at Swansea and elsewhere, and I have never failed to discover shots of regulus on the freshly fractured surfaces of the slag.

3. The *granulated coarse-metal* from No. 2 is calcined, with free access of air, in a calciner. It is frequently stirred and turned over. The operation is generally completed in about 24 hours, and towards the end the temperature is gradually raised.

4. The *calcined granulated coarse-metal* from No. 3 is melted, with the addition of matters rich in oxide of copper, namely, *roaster* and *refinery slags*, from the two remaining operations, Nos. 5 and 6, respectively, and *native carbonates of copper*, or ores containing *oxide of copper*. The products are a regulus, termed *metal*, which contains about 75 per cent. of copper, and *metal-slag*, which is melted in No. 2. The regulus should be in the state of *white-metal*. The slag is skimmed off and drawn out of the furnace through the end opening, below which sand-moulds are prepared to receive it. The regulus is tapped off into sand-moulds, similar to those above described, immediately in front of, and below, the tap-hole in the side of the furnace. When the regulus has become more or less pasty during the process of cooling, its surface is thrown up into little craters, caused by the escape of gas.

5. This operation is termed *roasting*. The pigs of regulus from No. 4 are introduced into a furnace similar in construction to a melting-furnace, with the exception that air is admitted through the fire-bridge, on Sheffield's plan, or through an opening in the side of the furnace near each end of the fire-bridge. The products are *roaster-slag*

and *blister-copper*; which contains about 95 per cent. of copper. The temperature is so regulated that the pigs may be completely melted in from 6 to 8 hours, and during this time air is allowed to circulate freely through openings in the sides of the furnace. The surface of the melted regulus presents the appearance of ebullition, and emits a frizzling sound. The slag which is formed on the surface of the melted regulus is skimmed off twice during the operation; the first time immediately after fusion, and the second just before tapping. After the operation has been continued during a certain time the temperature of the furnace is lowered sufficiently to allow the regulus to solidify. When the regulus has become pasty during the process of solidification, its surface is thrown up into craters—or in technical language "it rises"—owing to the continued evolution of gas, just as is the case mentioned under No 4. The regulus is again melted and tapped into sand-moulds. Before the end of the process the side-openings are closed, and an experienced workman knows exactly when this should be done. The blister-copper is tapped into sand-moulds.

6. This is the last operation, and is termed *refining*. The products are *marketable copper* and *refinery slag*. The furnace employed is similar in construction to a melting-furnace, with the following differences:—the bottom inclines gradually from all sides towards the deepest part, which is near the end door; there is a large door in one side, but there is neither a hole in the roof nor a side tap-hole. From 6 to 8 tons of pigs of *blister-copper* are introduced into the furnace through the side door, melted, and in this state kept exposed during about 15 hours to the oxidizing action of the air which enters the furnace. The slag is skimmed off through the end opening. The copper should be now in the state of *dry-copper*, that is, as has been previously fully explained, saturated with dioxide. The refiner takes out a small quantity of the copper in a little iron ladle and, according to the appearance of its fracture, judges whether the process of oxidation has been sufficiently prolonged. When he finds that it has, he proceeds with the process of *toughening* the copper. The metal having been well skimmed, anthracite or free-burning coal, as pure as can be obtained, is thrown upon the surface. Charcoal was formerly employed for this purpose. After a short time the thick end of a long birch or oak pole—the greener the better—is plunged into the melted copper and kept depressed therein by fixing a prop under the other end, which protrudes beyond the outside of the furnace. This part of the operation is termed *poling*. The wood in contact with the copper is rapidly decomposed; much gas and vapour are evolved, which cause the metal to be splashed about, and every part of it to be exposed to the reducing action of the coal upon its surface. The refiner takes out a small quantity of the metal, or *proof*, from time to time, examines the appearance of its fracture, and tests its qualities in the manner described at p. 226. When he finds it to be at the state of *tough-pitch*, the pole is taken out and the coal pushed back from the end opening, through which it is then laded out as quickly as possible and cast into suitable moulds. Should the metal during the process of lading

become more or less *dry*, poling for a short time is again resorted to; and should the poling be continued too long, and the copper become more or less *overpoled*, its surface is uncovered and exposed to oxidation during a short time. The copper is laded out by means of long-handled iron ladles coated with clay, which contain about 30 lbs. weight of metal each. The process of poling lasts about an hour and a half, including the time the coal remains on the surface of the metal, and that of lading requires about the same time. But the time of poling will depend, to a certain extent, on the state of the furnace. Copper is occasionally granulated by lading it into cold water, and in this state it is known as *feathered shot*, for which there was once a large demand by the makers of *calamine brass*. The copper for this purpose was overpoled when laded; the pieces are ragged, and resemble those of granulated zinc. It is also prepared in the form of more or less rounded pieces, in size and form resembling large beans, called *bean-shot*, which is produced by simply lading the copper into hot water. I should have thought that much would have depended on the height from which the metal was allowed to fall through the air before it reached the water, upon its temperature, and upon the volume in which it was poured. Melted copper in the overpoled state has a bright resplendent surface, which, like a mirror, reflects every brick of the furnace above. When the copper is intended for rolling, a certain quantity of lead is well mixed with it just before lading. The quantity required to produce a sound casting with a flat surface is variable, and depends much upon the degree of purity of the copper. When antimony is present in larger proportion than usual, it is affirmed that the amount of lead should be considerably greater. At one establishment the proportion was about 80 lbs. of lead to 6 tons of copper, while at others from 14 to 30 lbs. were added to this quantity of copper. The addition of lead to copper in order to render it malleable and ductile is an old practice.

Modifications of the Welsh process of copper-smelting.—I shall now describe as concisely as I can certain modifications of the process in operation at different works which I have visited. I have received permission to publish this information, with the single reservation of suppressing the names of the works. I shall retain the precise phraseology in use at the works in question.

First modification, as practised in 1859.

1. Ore calciners.—The raw ore is calcined during 12 hours, stirring every two hours.

2. Ore furnaces.—The charge is 21 cwts. of calcined ore from No. 1, and from 2 to 5 cwts. of sharp slag from the second fusion. It is melted in 4 hours, when the door is taken down and the contents of the furnace well stirred; the door is then put up, and in a quarter of an hour afterwards is taken down, when the slag is skimmed off and the metal tapped into water or sand. According to the smelter, a man of great experience, who furnished me with this information, the coal employed in the ore furnaces should not be too clean in order that a good clinker bed may be formed. The same smelter considers that a

mixture of ores containing from 7 to 8 per cent. of copper is the best for smelting.

3. Metal calciners.—The raw or granulated metal from No. 2 is calcined during from 24 to 30 hours, stirring every second hour.

4. Coarse-metal furnaces.—The charge is, calcined metal from No. 3 20 cwts., fine-metal and roaster-slags 4 cwts., and carbonates 3 cwts. It is melted in 6 hours, when, after skimming the slag, the melted metal is tapped into sand.

5. Fine-metal furnaces.—The charge is, coarse metal from No. 4 24 cwts. and refinery slag 2 cwts. It is melted in 6 hours and tapped into sand.

6. Roasting.—The charge of fine-metal from No. 5 should be sufficient to yield 2 tons of copper. The heat is raised to the melting-point of the metal; the air (teasing) holes are now opened and the metal gradually melted down in from 6 to 8 hours; it is kept in a melted state during about 12 hours and then skimmed. If the fine-metal, now called for the first time *regule*, is all reduced to copper, the heat is raised, the metal well melted, and tapped out into sand as *pimple* or *blister-copper* as required. The whole operation of roasting requires 24 hours.

7. Refining.—The charge is from 5 to 7 tons of coarse copper (i. e. impure metallic copper). It is melted and air admitted at the side door. Black blisters rise to the surface of the metal and burst. The copper is well rabbled all the time. If the charge is of *pimple-metal*, a pole is put in to agitate and expose it to the action of the air; when the copper ceases to "work," it is allowed to set; it is afterwards again melted and skimmed. The refiner now takes the charge, and the poling commences. When necessary—as he judges from the assay which he takes out—from 16 to 20 lbs. of lead are thrown in and well stirred with the copper, and the door is put up, after which the charge is skimmed and covered with charcoal or stone-coal (anthracite). Some of the copper—or a "trial"—is now beaten out, and, if the result is satisfactory, the lading begins, during which the refiner constantly takes out "assays," and regulates the pitch-copper accordingly by throwing in a piece of pole or admitting air till the charge is all laded out. The whole process of smelting lasts from 70 to 96 hours.

At these works from 13 to 18 tons of coal, which now (1859) costs five shillings a ton, are required to make one ton of copper, and about the half of this quantity is consumed in the first and second operations of calcining and melting. A mixture of three parts by weight of free-burning and one of binding coal is employed.

Second modification, as practised in 1859.—The mixture of ores employed contains, on an average, 9 per cent. of copper, as determined by the Cornish method of assaying.

1. Calcination.—The large calciner, of which engravings are given (pp. 314-16), is employed; it holds 7 tons of ore; the process lasts from 12 to 24 hours.

2. Ore furnace.—The charge is—*calcined ore* from No. 1, 22 cwts.

(1 cwt. = 112 lbs.) and 6 of metal or sharp slag. The products are—metal, which is granulated, and ore-furnace slag, which is thrown away.

3. The *granulated coarse-metal* from No. 2 is calcined during from 15 to 18 hours.

4. The charge is—*calcined granulated coarse-metal* from No. 3, 45 cwts., with 6, 9, or 12 cwts. of slag from No. 6, and roaster-slag or native carbonates of copper, according to circumstances. The products are *fine-metal*, which is granulated, and slag.

5. The *granulated fine-metal* from No. 4 is calcined during 18 hours.

6. The charge is—*calcined granulated fine-metal* from No. 5, 50 cwts. and *refinery slag* only from 3 to 6 cwts. The products are—*fine-metal* (still called only *fine-metal*) and slag. The metal obtained in this operation may occur in the state of *blue-metal* or *pimple-metal*. The Welsh name for the last metal is crych, which means rough; the surface of the metal being rough from pimple-like excrescences. When the metal is still further advanced beyond the state of *pimple-metal*, it is called *close regule*, which almost always contains metallic copper.

7. Roasting.—The charge is—*fine-metal* from No. 6, 2 tons. It is heated at first rapidly and then melted down, so as to require 4 hours for complete fusion, after which the slag is skimmed off through the front door—the opening near the stack being commonly called the front of the furnace. The side door is then opened in order to admit the air freely; this opening into the furnace is near the fire-bridge on one side. The metal is kept in a melted state during 18 hours. It is skimmed twice, or oftener, according to circumstances, during the process of roasting. Towards the latter part of the operation, the heat of the furnace remaining constant, the metal becomes what is termed "dead," i. e. more or less set or solidified at the surface. In proportion as the impurities are removed, a higher temperature is required to maintain the state of fusion. The heat is finally increased by closing the side door so as perfectly to fuse the contents of the furnace. The product is *blister-copper*, which is tapped off.

8. Refining.—The charge is from 6 to 7 tons of blister-copper. The copper is kept melted during 18 hours, and is skimmed about three times at intervals; it receives one good skimming after it is thoroughly melted down, and another before throwing on the "fluxing" coal preparatory to poling. Free-burning coal is used in this process, and is left on the surface of the metal during the whole time, including that of lading. Generally at these works the fuel employed consists of two parts by weight of free-burning and one of binding coal. With some kinds of coal equal weights are used.

Third modification.

1. Melting.—The mixture of ores employed contains, on an average, 9 per cent. of copper. It is melted without previous calcination. The charge is, mixed ores 22 cwts. and sharp slag 4 cwts. The products are, ore-furnace slag, which is thrown away, and metal, which is first granulated and then all passed between rolls, by which means it is reduced to small particles. It is said to contain as much as 38 per cent. of copper.

2. Calcination.—The charge is 5 tons of *crushed granulated coarse-metal* from No. 1, and the calcination is continued during 24 hours.

3. Second melting.—The charge is *product of No. 2*, 36 cwts., *roaster* and *refinery slags*, and *native carbonates of copper*, together 3 cwts. The products are *blue-metal* and *sharp-slag*.

4. The *blue-metal* from No. 3 is roasted to *pimple-metal;* the charge is 4 tons. The products are, this metal and *coarse roaster-slag*.

5. The *pimple-metal* from No. 4 is roasted to *pimple-copper;* the charge is 5 tons. The products are, this copper and *roaster-slag*.

6. Refining.—The charge is about 8 tons.

In the preparation of *tough-cake* copper about 35 lbs. of lead are added.

The ore is raised by a hydraulic lift and conveyed in waggons direct to the ore-furnaces on a railway, which is constructed on the outside round these furnaces and on a level with their tops. By this arrangement labour is much economised.

The process of making "best selected" copper.—I am indebted for the following historical notice of the introduction of this process to my friend Mr. Keates.

"*Best selected*" is a comparatively modern term, *Best* being the old term. The introduction of the manufacture of brass on a large scale into this country does not date much further back than the year 1680, and the manufacturers were not long in discovering that copper taken indiscriminately as it occurred in the market frequently produced brass quite unfit for manufacturing into battery, sheets, and wire, and they rightly attributed this to its impurity. The English copper generally in use at the beginning of the 18th century was derived from Cornish ores, which were then, to a greater extent than at present, mixed with tin; and it is most creditable to the sagacity and practical skill of the smelters of that day that they devised a mode of remedying the evil which, in effect, has not been improved upon by their successors. The following "Directions for taking out the second or common copper so as to make best copper for brass" date about the year 1743, and were in manuscript, but no doubt had been practised years before:—

"In the first place you must calcine the ore for a certain time, so that, when smelted, the metal from it when broken appears of a brownish colour tinged with blue; in general ten or twelve hours will be sufficient. When you smelt the ore if you find it melts very liquid I would advise to tap out the contents instead of skimming, and you will find the metal in one, two, or three of the first pigs, according to the quantity of it; which metal must be drawn aside and a quantity of cold water thrown upon it until it begins to crack and fall to pieces, and in this manner you must proceed until you have got metal enough for the next operations. But if the ore does not melt very thin, then you must skim off the slag and tap out the metal, and quench it with water as before directed. You must always endeavour to keep your metal in the afore-mentioned pitch, so that, when the water is thrown upon it while hot, it will fall to pieces like a lump of quick-lime, and not require to be buckered to pieces. You must now take your metal

to the calciner and calcine it for such a length of time as, when it is melted, will give you a little bell-metal in the runner-pig. Twelve or fourteen hours will generally do to calcine. When the metal is calcined, take enough of it for a charge for the metal, or regule, furnace, to melt in four or five hours, and add to it a box or two of refinery-slag pounded down small, and also two or three boxes of good thin slag and two or three shovels of cokes or cinders. When this mixture is properly melted, tap it all out of the furnace together and the metal will be found in five or six of the first pigs, and at the bottom of the runner-pig will be found a quantity of whitish-looking metal called bell-metal, and this must be separated from the metal, or regule. The regule is then taken to the roaster-furnace and roasted such a length of time that, when tapped out, there shall be found at the bottom of the pigs four or five hundred-weight of coarse and common copper, which is separated and kept for inferior purposes. The regule, which now begins to get hollow and spongy, is kept to make the best copper, which it does when roasted."

The term "*bucker*" means to pound or bruise with hammers into small pieces. "*Runner*"-pig is the pig or mould in the bed of sand into which the metal first runs from the tap-hole.

Modifications of the process of making "best selected" copper at different works in 1859.

1. This method is practised at the works where the *first modification* (p. 326) is carried on. About two tons of *fine-metal* (from the third fusion) are melted down, and roasted during a certain time according to the judgment of the furnace-man. When ready the contents are tapped into sand-beds, or moulds (made as described at p. 324); from five to seven pigs of reduced impure copper will be found in the moulds nearest the tap-hole; and from the surface of these pigs the *regule* is stripped off immediately on its setting. The total number of pigs may be about eighteen or twenty, according to the size of the sand beds. About one-fourth of the copper is reduced in this first melting in making *best-selected* copper. The *regule* thus obtained is again treated in the manner just described, when about the same proportion of copper will be abstracted as impure, so that in the two meltings about half of the total quantity of copper is reduced. In this reduced copper, termed "bottoms," certain impurities, especially tin, will be found concentrated. That produced in the second melting is roasted to *blister-copper*, which is refined in the usual way. The usual proportions which should be obtained when common ores are treated are about eleven tons of *best-selected* copper and nine tons of *bottoms*. These bottoms are cast into small rectangular tile-shaped pieces, which are known in the market as "tile-copper;" or, according to the necessities and opportunities of the smelter, they may be cast into *cake-copper*.

2. At the works where the large calciner was used (*second modification*, p. 327), I obtained the following information: The *selecting* process follows No. 6. The product of No. 6 is roasted, so that about half the copper which it contains may be reduced. The residual

metal is termed *regule, best regule*, or *spongy regule*. It is afterwards roasted and refined by itself.

3. This method is adopted at the works when the *third modification* (p. 328) is carried on. *Best-selected* copper is prepared from *pimple-metal*. When this metal is tapped into sand-beds in the usual way, eight or ten pigs nearest the tap-hole are put aside for *tough-cake* copper, and the remaining pigs, about fourteen in number, are reserved for the *selecting process*. The pigs put aside contain metallic copper in strings; and at these works the roasting is not carried so far as to cause a distinct separation between the *bottoms* and *regulus*. The pigs used for selecting are in the state of *close*, not *spongy*, *regulus*. The furnace is charged with about five tons of *pimple-metal* pigs; the furnace-doors are then closed until the metal becomes red-hot, but not melted. The air is now freely admitted into the furnace through holes, termed "port-holes," of which there is one on each side near the fire-bridge. The temperature is so regulated that the pigs may be sweated down in six hours; the port-holes are now closed, and the metal becomes thoroughly melted in the course of three hours, when it is skimmed. One of the port-holes is opened, and the charging-door at the side partially. The regulus is thus left until it is converted into *rough-copper*. The side-door and port-hole are now closed until the contents of the furnace are well melted; after which the tap-hole is opened, and the metal obtained sent to the refinery.

As large quantities of *concentrated regulus* as well as *cake copper* have been imported from South America to this country, the following description of the method of smelting which was practised by the Mexican and South American Company may be interesting. I received it from the furnace-manager of the company, Mr. M'Auliffe, who was for some time a student in the Metallurgical Laboratory of the School of Mines.

Copper-smelting in Chili.—The smelting was effected in reverberatory furnaces with coal from this country.

1. *Fusion for regulus.*—One charge consists of 70 quintals (over 3 tons English), and is composed as follows:—

Ore.	Locality.	Quintals.	Average per centage of copper.
Carbonates and oxychloride (green and dark brown)	Caldera	12	12
Silicate	Tongoy	8	10
Iron fluxes from various parts of	Coquimbo	14	8
Limestone		4	3
Carbonates and oxychloride; hard to be fused; containing a good deal of "*Tofo*" (chiefly carbonate of lime)		2	8
Sulphides (blue)	Tongoy	6	20
,, (yellow)	Various places	6	8
,, (yellow)	Totorallillo	16	8
Roaster slag		2	9
Total quintals		70	

Each furnace smelts four charges in 24 hours. The regulus contains about 60 per cent. of copper; and the slag, which is "sharp" and brittle, is said rarely to contain more than 1 per cent. of copper.

2. *Roasting for spongy regulus.*—A charge of 4 tons is roasted during about 8 hours; the time from charge to charge, inclusive of charging, tapping, &c., is 10 hours. Out of 20 pigs of the *spongy regulus* (metal) about 6 or 8 have "bottoms." The *metal* is not allowed to become too spongy, as in that state it would become mixed with too large a quantity of sand, which it is stated would retard the next roasting. The slag contains 9 per cent. of copper.

3. *Roasting for blister-copper.*—The charge consists of sufficient spongy regulus and "bottoms" to yield from 4 to 5 tons of *blister-copper*. The time required to work off the charge is from 16 to 18 hours. This operation of *roasting* is conducted as follows:—The charge is first allowed to *sweat* down, which requires about 6 hours, when the air-holes are luted and the temperature raised, so that the whole charge may be perfectly melted in 1 hour. The front door is now taken down and any slag that may have accumulated is skimmed off, after which the charge is allowed to set by opening the side door and air-holes. As soon as it is quite *set*—or before, if the copper can easily be seen by striking back the "rigole" (regulus) floating on the surface of the bath, with a skimming rabble—the side door is luted and the temperature gradually increased until the whole charge is in a state of fusion. During this period the two air-holes are left open, but too much air must not be admitted, as the charge would be thereby prevented from melting. If the furnace has had proper attention, and the charge is "working" (*i. e.* appears to boil), it continues in this state from 30 to 40 minutes. The "working" ceases first in those parts near the air-holes, and soon afterwards in every part of the furnace, the surface becoming covered with a thick yellow coat called "cream," from which small blisters about the size of a pea are thrown up. The *blister-copper* is now tapped into sand moulds. After the second fusion, or before the charge begins to work, any slag covering the face of the bath should be skimmed off.

Three furnaces are used. In an establishment of 9 furnaces, 6 smelting-furnaces will keep the 2 "roasters" continually going; but this depends on the per centage of copper in ores used.

On the Re-actions which occur in the Welsh Process of Copper-smelting.

Le Play, formerly Professor of Metallurgy at the École des Mines at Paris, has published an elaborate description of the process, and the results of an analytical examination of the products which are formed in each operation.[b]

His information was chiefly obtained at the Hafod Works, where, I am informed, he would frequently remain at the furnaces from morning till night. Mr. James Napier subsequently communicated to the 'Philosophical Magazine' a series of papers on this process of copper-smelting.[1] He resided at Swansea, and was engaged at the Lougher

[b] Description des Procédés Métallurgiques employés dans le Pays de Galles pour la Fabrication du Cuivre. Paris, 1848, pp. 496.

[1] Fourth Series, 1852, vol. 4, pp. 45, 192, 262, 345, 453. Vol. 5, 1853, pp. 30, 175, 345, 486.

or Spitty Copper-works, when I visited them in 1848. In the following pages I shall freely avail myself of the writings of both the authors above-mentioned.

Calcination.—Atmospheric oxygen, aided by heat, is the essential agent in this operation. In order to understand the re-actions which occur, the composition of the ore *before*, and *after*, calcination should be ascertained; but, according to Le Play, the changes effected in the chemical composition of the ore by calcination cannot be completely revealed by comparative chemical analyses of the raw and calcined ores; because, owing to the mechanical mixtures of several sulphides and oxides in different degrees of sulphuration and oxidation, the data obtained by such analyses do not suffice for the calculation of the exact proximate composition of the ore. That this problem may be difficult of solution from the cause assigned by Le Play, is probable; but that it should be incapable of solution, even by an experienced analyst, may fairly be questioned. However, Le Play believes he is able to explain the re-actions which occur in the process in question, so as very nearly to approximate to the truth.

Some of Le Play's results are presented in the following table, which is extracted from his work:—

Composition of the Raw Ore.		Composition of the Calcined Ore.	
Dioxide of copper	0·4		5·4
Copper-pyrites	22·7		11·2
Iron-pyrites (FeS^2)	22·4	Sesquisulphide of iron (Fe^2S^3)	11·2
Various sulphides	1·0		0·6
Sesquioxide of iron	0·6		11·7
Various oxides	0·3		0·6
Silica	34·3		34·3
Earthy bases	2·0		2·0
Water and carbonic acid in the state of combination	0·5	Sulphuric acid combined	1·1
	84·2		78·1
Atmospheric oxygen consumed by this amount of ore in the process of calcination	15·8	Evolved as gas: Water and carbonic acid	0 5
		Evolved as gas: Sulphurous acid	21·4
	100·0		100·0

The loss of weight which occurred during calcination was found to be 7·2 per cent., and the loss of sulphur 51·9 per cent. of the total in the ore.

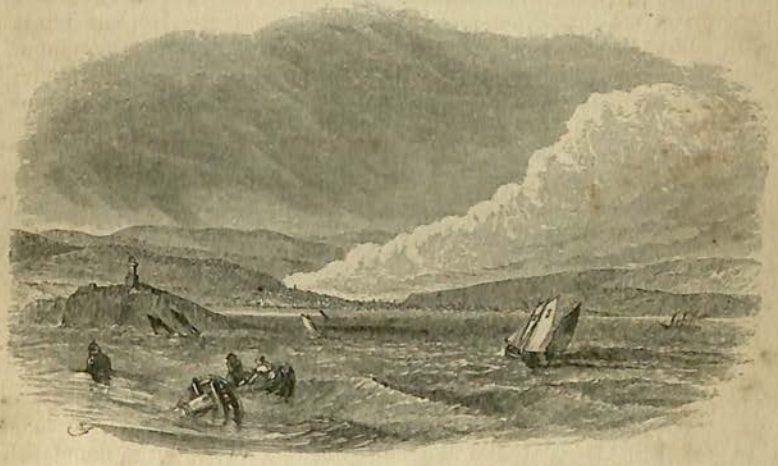
The chemical changes which occur when disulphide of copper is heated with free access of air have been previously considered. When copper-pyrites ($Cu^2S+Fe^2S^3$) in a finely-divided state is heated under the same conditions until no further evolution of sulphur in any state takes place, even when the temperature is raised to bright redness, the product will consist of a mixture of protoxide of copper and sesquioxide of iron. Sulphate of copper is formed and afterwards decomposed, just as in the calcination of disulphide of copper. A sulphide of iron may, in like manner, be converted into sesquioxide: sulphate of protoxide is formed and decomposed with the formation of sulphate of sesquioxide, from which the sulphuric acid may afterwards be wholly expelled. Le Play estimates the whole of the oxide of iron

in the calcined ore as sesquioxide; but if I mistake not, some magnetic oxide of iron at least will always exist in the calcined ore, when any sensible amount of the sulphides of copper and iron is left, as is invariably the case in the calcined ore of copper-works. The calcined ore which I procured from the Hafod Works contained a considerable quantity of black matter, capable of being separated by the magnet; small lumps were picked out of this ore, consisting of minute, loosely-aggregated, brilliant black crystals, which under a lens were found to present triangular faces, were attractable by the magnet, and dissolved without effervescence in hydrochloric acid, producing a solution containing proto- and sesqui-chloride of iron: so that the crystals were evidently magnetic oxide of iron. The presence of a sulphide of iron promotes the oxidation of disulphide of copper during calcination; because the former sulphide is more easily oxidized than the latter, and the resulting sulphate of protoxide of iron may, by its subsequent decomposition, produce the same kind of oxidizing action as is caused by the decomposition of sulphate of copper in the manner described at p. 249. When iron-pyrites is present the same re-actions take place, the only difference being that part of the sulphur burns with a blue flame, like free sulphur, and evolves a considerable amount of heat. When iron-pyrites containing copper-pyrites is roasted under certain conditions, not in a state of fine division, but in lumps, curious phenomena are observed, which will be particularly explained hereafter.

It will be remarked, sulphur is only partially expelled: it escapes chiefly in the state of sulphurous acid, which, in certain directions of the wind, may be tasted in every house in Swansea; and it is also evolved to a certain extent in the state of sulphuric acid. Le Play detected the presence of this acid in the smoke of the ore-calciner at all periods of the calcination, by keeping moistened tow, which had been carefully washed with distilled water, in the smoke for some time; the tow was afterwards digested with water. When chloride of barium was added to the solution thus obtained, copious turbidity followed, which was not removed by hydrochloric acid. In 1822 Mr. Faraday and the late Mr. Richard Phillips found sulphuric as well as sulphurous acid in water which had been well exposed to contact with the smoke from the ore-calciners at the Hafod Works; and yet in their analysis of this smoke, before it came in contact with water, there is no mention of the presence of sulphuric acid.[2] Le Play makes the singular remark "that the prevailing taste of the gas in the Welsh smelting-works is by no means (nullement) that of sulphurous acid; but is precisely that of those thick vapours which disturb the transparency of the air in laboratories where sul-

[2] Proceedings of the Subscribers to the Fund for obviating the Inconvenience arising from the Smoke produced by Smelting Copper Ores; Report of the Judges who decided on the Merits of the Trials submitted to their consideration; and Statement and Plan explanatory of the Experiments made at the Hafod Works: with an Account of the Process of Smelting Copper, etc., 8vo. pp. 95. Swansea, 1823.

phuric acid is evaporated, or sulphates are decomposed."[3] However, according to my experience, the prevailing taste of the gas of these works is certainly that of sulphurous acid; but *de gustibus*, &c. It is, I believe, a common observation at Swansea and in the neighbourhood that the copper-smoke is rendered much more opaque by rain; and this may, probably, be due to the fact that the sulphuric acid, which is produced by the decomposition of the sulphates of iron and copper, passes into the atmosphere, partially at least, in the state of anhydrous acid, which, as is well known, causes dense white fumes when exposed to moist air. It is true that the gaseous products of the combustion of the coal and the air which finds its way through the sides or bridge of the furnace, pass over the ore, and both contain aqueous vapour; yet, from one cause or other, some of the anhydrous sulphuric acid evolved may issue from the top of the stack into the atmosphere. In special cases there may be other conditions which tend to increase the opacity of the copper-smoke. A dense cloud of this white smoke perpetually hangs over the copper-works of Swansea and the vicinity, and



Swansea, as seen at Sea near the Mumbles.

occasionally beautiful effects are produced in the landscape when the rays of the sun fall upon it, especially towards evening. In favourable states of the atmosphere, I have frequently seen it with the utmost distinctness at Lynton, which is situate on the south side of the Bristol Channel, at a distance of twenty-seven miles in a direct line from Swansea.

Le Play remarks that the opacity of the sulphureous vapours evolved during calcination of the ore is never greater than at the moment when it is taken out of the furnace; and at first he concluded that the proportion of sulphates contained in the calcined ore would be very

[3] Op. cit., p. 163.

considerable. However, he found that while the proportion of sulphuric acid never exceeded 2·2 per cent. in any ore, many ores contained not a trace; and this trace, he believed, existed in combination with lime and magnesia, rather than the metallic bases. The amount of sulphuric acid which may exist in combination with these bases in the calcined ore depends entirely on the degree of heat to which it has been exposed: of this ample proof, if any were required, will be found in the sequel.

According to Favre and Silbermann, some anhydrous sulphuric acid is produced by the direct combustion of sulphur in oxygen gas, and an almost imponderable quantity of this acid suffices to render a very large volume of air opaque.[4] But I am not aware that the transparency of the atmosphere is affected by the burning of sulphur either in large or small quantity, which would be the case if anhydrous sulphuric acid were formed, even in minute proportion.

Mr. Napier has published the following statements relating to the process of calcination, which, in my judgment, cannot be accepted. "We took," writes Mr. Napier, "a charge of Cuba ore and calcined during twelve hours, and tried every hour, gave the following results" (*sic*).

Composition of the Ore.

	When put into the furnace.	In 1 hour.	In 2 hours.	In 3 hours.	In 4 hours.	In 5 hours.	In 6 hours.	In 7 hours.	In 8 hours.	In 9 hours.	In 10 hours.	In 11 hours.	In 12 hours.
Copper	12·3	13·0	12·2	12·2	13·0	12·2	13·8	12·6	12·6	12·5	13·2	13·8	12·2
Iron	32·7	30·0	24·4	32·8	28·7	31·3	33·6	30·6	30·0	27·6	24·3	40·3	27·0
Sulphur	31·1	28·3	23·6	18·6	29·2	24·4	12·2	18·1	20·0	15·9	18·8	17·5	16·2
Silica	24·0	28·0	32·0	28·0	26·0	28·0	34·8	32·0	30·0	30·8	33·0	21·0	40·0
	100·1	99·3	92·2	91·6	96·9	95·9	94·4	93·3	92·6	86·8	89·3	92·6	95·4

Mr. Napier remarks: "when we take into consideration the several amounts of sulphur, we observe what appears very anomalous—that there is less sulphur at the end of six hours than after twelve. It may be asked, where the sulphur is gone, whence comes it again? In all our experiments this intermitting action of the sulphur is exhibited."[5] He then presents, in rather unintelligible language, an explanation of this alleged action. Now, in another experiment, the results of which are given in the very same paper as that from which the preceding extracts were taken, Mr. Napier found that the sulphur gradually diminished from the commencement to the end of the calcination, which was continued during forty-four hours. But we hardly seem to require the aid of experiment to demonstrate the fallacy of the "intermitting action." It is certain that during the entire period of calcination sulphur, especially in the state of sul-

[4] Ann. de Chimie et de Phys. 3 s. 1852, 34. p. 445.
[5] Phil. Mag. 4 s. 1852, 4. p. 459.

phurous acid, issues in a continuous current from the furnace; and as this sulphur must be derived from the ore, except the comparatively minute and quite insignificant amount which may be evolved from the fuel, it follows necessarily that its proportion in the ore must continually decrease from the beginning to the end of the process. In order that Mr. Napier's results should be of any value, it is essential that the ore operated upon should be absolutely homogeneous throughout, and that every portion withdrawn from the furnace for the purpose of analysis should be a *perfect sample*: in other words, a specimen which, for the time being, correctly represents the average composition of the ore; but it must obviously be extremely difficult, especially when operating upon large quantities of ore in furnaces, to ensure this indispensable condition; and it may be proved from the very data which led Mr. Napier to admit "the intermitting action" in question that the successive portions of ore which he extracted from the calcining furnace, and afterwards analysed, could not have been samples. If the specimens successively taken out of the furnace had been *samples*, the ratio between the *fixed* constituents, namely, silica, copper, and iron, should obviously be the same in each. But on referring to the table of results above inserted, we find that such was not the case. Let us compare the ratios between the silica and copper: in the ore before calcination it was 100 : 51; in 1 hour, 100 : 46; in 2 hours, 100 : 38; in 4 hours, when the sulphur increased from 18·6 to 29·2 per cent., 100 : 50; in 6 hours, when the sulphur decreased from 24·4 to 12·2 per cent., 100 : 39; in 11 hours, 100 : 65; and in 12 hours, 100 : 30.

When the mixture of ores smelted contains iron-pyrites, as is generally the case, free sulphur may be volatilized during calcination; for iron-pyrites, when heated to redness, loses about half its sulphur. Faraday and Phillips found a little sulphur deposited from the smoke of the ore-calciner at the Hafod Works.[6] Mr. Napier remarks that "sulphur will not sublime freely from ores in an atmosphere of sulphur," and alludes to a "law" which "must be attended to in all subliming operations."[7] I have never found any difficulty in subliming free sulphur in a flask, or volatilizing sulphur from iron-pyrites when heated in covered crucibles.

Composition of the gaseous products which escape from the ore-calciner.—Faraday and Phillips made two analyses of the air from the ore-calciner flue at the Hafod Works: their results are as follow.[8]

	1.	2.
Sulphurous and carbonic acid gases, absorbable by water	10·64	9·28
Oxygen	8·94	9 66
Nitrogen	80 42	81·06
	100 00	100·00

These results are interesting, as showing that a considerable amount of *free oxygen* exists in the gases which issue from the calciner. I am

[6] Op. cit., p. 61. [7] Phil. Mag. 4 s. 4. p. 462. [8] Op. cit., p. 64.

not aware whether the composition of these gases has again been investigated by any competent chemist.

Total amount of sulphur annually evolved from the copper-works of Swansea and its vicinity.—We are indebted to Le Play for the following calculations: Sulphurous acid forms 21 per cent. of the total weight of the sum of the fixed and volatile products of calcination, and 25 per cent. of the weight of the ore subjected to calcination: the weight of sulphur contained in this gas amounts to 13 per cent. of that of the ore. During the entire process of smelting, the sulphurous acid and sulphur expelled amount, respectively, to 56 and 23 per cent. of the weight of the ore. The total weight of copper-ore smelted in South Wales (some time before 1848) being about 200,000 tons, about 46,000 tons of sulphur were annually volatilized, producing 92,000 tons of sulphurous acid.[9] In the works situate near Swansea, nearly two-thirds of the ore imported into South Wales are smelted, so that daily 65,900 cubic metres of sulphurous acid are projected from these works into the atmosphere. This acid being very hurtful to vegetation, not a blade of grass will grow on the neighbouring hills, which are particularly exposed to its influence. The sulphuric acid contained in the copper-smoke is, probably, more injurious than the sulphurous acid, as every drop of rain, in falling through the smoke, becomes a solution of oil of vitriol, which, alighting upon foliage, is rendered more corrosive by subsequent evaporation of a portion of the water.

The value of the sulphur annually dissipated in the atmosphere was estimated by Le Play at 200,000*l.*

Various attempts have been made to lessen the nuisance caused by the copper-smoke, and, at the same time, to turn to account the sulphurous acid which it contains, by applying it to the manufacture of sulphuric acid; and I believe large sums of money have been from time to time expended in the execution of schemes proposed with this object. But all such projects have hitherto proved unsuccessful. The proprietors of the Hafod Works forty years ago incurred a direct expenditure exceeding 6,000*l.*, exclusive of other indirect expenses, in attempting to abate the evil of the copper-smoke. The smoke was made to take a tortuous course through long flues and chambers, into which water was injected in numerous fine streams; and only the uncondensable portion was afterwards allowed to escape into the air from the top of a high stack. That the late Mr. Vivian believed these contrivances would prove successful is shown by the following extract from his pamphlet:—"And if we cannot flatter ourselves that we have absolutely, entirely, and effectually got rid of every particle of the matter which has been considered as producing inconvenience, we may at least affirm that we have abated it to a degree beyond the possibility of its producing, as far as our Works are concerned, future cause for complaint; and we feel confident that the liberality of the inhabitants of Swansea and the immediate vicinity of the Works

[9] Le Play uses the word *tonneau*, which is equal to 1000 kil., or about 1 English ton.

will do us the justice to believe that we have been stimulated in our endeavours to effect this, much more by a sincere desire on our parts to meet their wishes, and by a sense of *the advantages that would arise to the town and neighbourhood*,[1] than by the hope of benefiting ourselves or the fear of any proceedings against us in a court of law." This method, however, of condensing the smoke does not appear to have been attended with the success at first anticipated, if we may judge from the fact that it was soon abandoned, and the Hafod Works still contribute their full share of copper-smoke to the general stock.

Quite recently an energetic inhabitant of Swansea has endeavoured to apply the existing law concerning the suppression of smoke to the particular case of copper-smoke; and I am informed that legal authorities consider this kind of smoke as exceptional, possibly because it is *white*, and not *black*, like ordinary smoke. However this may be, the proprietor of the Patent Fuel Works at Swansea has been compelled at great expense to construct a long flue to the top of the Kilvey Hill, at the base of which the works are situated, in order to carry farther away some dark-coloured, foul-smelling smoke, which is intolerable to the inhabitants of a town who can submit without a murmur to the sulphureous and choking exhalations of the copper-works.[2] Nay, it has, I understand, even been gravely maintained by some persons that copper-smoke is beneficial, if not agreeable, rather than otherwise. This, however, was assuredly not the opinion of the late Member for Swansea, Mr. Vivian, who, in opposition to his own interest, had the honesty to declare that the suppression of the smoke would be advantageous to the town and neighbourhood; nor does it appear to be the opinion of the existing smelters, if we may judge from the fact that, with scarcely an exception, they have selected residences which the smoke cannot reach. The smoke is an unmistakeable nuisance; and the man who pretends that it is not, must either have a peculiar constitution or lie under some strange delusion.[3]

That the smoke may be conveyed to a considerable distance without injuriously affecting the working of the furnaces, may, I think, be reasonably inferred from the following facts: 1. The experience of the late Mr. Vivian proved that at least several calciners might

[1] Op. cit., p. 49. The italics are not in the original.

[2] The flue is egg-shaped, 4 ft. 3 in. wide by 4 ft. 9 in. high. It is about 850 yards in length, and terminates in a stack 50 ft. high, of which the top is 400 ft. above the furnaces at the works below.

[3] In 1854 Dr. Thomas Williams, of Swansea, published a "Report on the Copper-Smoke, its Influence on the Public Health, and the Industrial Diseases of Copper-men." The following extract is a fair specimen of the style of the author:—"The furnace-chimneys of the copper-works, thousands (?) by number, emit gracefully-gyrating, white, smoky, and fleecy columns, which circlingly and wideningly ascend to the upper regions of the atmosphere, thereat to be lost in the purity of invisible air, or, marrying art to nature, to be mingled with the clouds."—p. 10. The author intimates at p. 4, that in consequence of the direct action of the copper-smoke during twenty years ague has ceased to prevail over certain marshes near Swansea; whereas at p. 12 he intimates that the suppression of malaria is due to the filling up of a tidal morass by enormous accumulations of slag.

advantageously communicate with a single stack. 2. At the Cwm Avon Copper-Works, 42 furnaces (I believe all, except those of the refinery) are connected with only one large chimney. This chimney runs up the side of the adjoining hill, where, on the top, it rises vertically 40 feet from the ground, forming a stack: its length, from the works to the top, inclusive of the stack, is 1100 yards; and its height, above the level of the works to the top of the stack, is 1100 feet; its internal diameter is 13 feet. The stack is a most conspicuous object in the landscape on all sides, and may be seen at a great distance. The hill on which it is erected is more or less conical; and the stack not being visible from the low ground of the surrounding country, the smoke appears to issue from the top of the hill, which in certain aspects might be mistaken for an active volcano. In 1859 I ascended the hill, and found the summit for a considerable distance round the stack utterly devoid of vegetation: the plant which survived at the highest elevation was a small *eriophorum*. 3. At the Llanelly Copper-Works one stack is common to all the calciners. 4. At the Pembrey Copper-Works all the furnaces, with the exception of two refining furnaces, communicate with a single stack 270 feet high and 31 feet square on the outside at the base. It is built square to the top. Up to the height of 100 feet there are double walls, with a free space between them, into which air is allowed to enter through holes at the bottom: by this means the outer casing of brick-work is kept cool, and preserved completely from the action of the copper-smoke. I was assured at the works that the furnaces worked perfectly with this arrangement. 5. At the Spitty Works, where I am informed on good authority the process of copper-smelting was successfully carried on, so far as the furnaces were concerned, there was one large circular stack with which nearly all the furnaces were connected.

Now, although high stacks at the copper-works at Swansea might relieve the town from much of the smoke, yet they would doubtless be detrimental to the interests of the neighbouring landed proprietors, whose crops and trees would then be seriously damaged; the effect of a high stack being merely to deliver the smoke into the atmosphere at a great elevation, and so cause it to travel to a greater distance before descending to the ground. I fear that unless some economical system can be put in practice of extracting the noxious constituents of the smoke without in any degree interfering with the working of the furnaces, Swansea must continue to tolerate the nuisance; and she will probably console herself with the reflection that it is inseparably connected with a trade which has so largely contributed to her development and prosperity. Under any circumstances, should a method hereafter be discovered of suppressing the nuisance without inconvenience to the smelters, Swansea should in justice be required to contribute a fair share of any expenditure which it may be necessary to incur in putting that method in practice.

Mr. Grenfell informed me in 1848 that apparatus had been erected at his works at a cost of 2,000*l.*, under the direction of Schafheutl, of

Munich, with a view to employ the smoke as a source of sulphurous acid in the manufacture of sulphuric acid. But the result was a failure. Yet I am inclined to believe that the nuisance will not eventually prove irremediable; and that the desired end is most likely to be attained by following up the experiments made at Mr. Grenfell's works. In some localities significant improvements in reverberatory furnaces are already in operation, which consist essentially in rendering the draught of the furnace less dependent on the stack, by causing the air to enter by the direct application of mechanical power; and, if I mistake not, considerable progress has yet to be made in this direction. Whether the principle of thus supplying air is capable of being applied with advantage to copper furnaces can only be decided by experiments. Should it be found practicable, it will then be possible to expose the smoke to conditions much more favourable to the separation of its sulphureous constituents than when the draught of the furnaces is determined by the exhausting power of the stack alone. In the calciners especially, from which the greater part of the smoke is evolved, the velocity of the current of air through them is small as compared with that which passes through the melting furnaces; so that there would probably be much less difficulty in applying the principle in question to the former than the latter description of furnaces.

At the copper-works in the Isle of Anglesea, where pyrites ores are smelted, it has long been the practice to collect a considerable quantity of the sulphur evolved during the first process of calcination.

Of late soda-makers have largely employed Irish and Spanish iron-pyrites containing a small proportion of copper in the manufacture of sulphuric acid; and they have been accustomed to dispose of the residues of cupriferous oxide of iron to copper smelters. But I have recently been informed by a large firm in the North of England that they propose forthwith to erect furnaces for the extraction of the copper from these residues. It is not improbable that, should this project be found successful in a pecuniary point of view, the combination of copper-smelting with the manufacture of sulphuric acid may become pretty general. The utilization of the sulphur for this purpose would render copper-smelting comparatively innocuous to vegetation, and allow of its establishment in districts where at present it would not be tolerated. Moreover, the profit derived from the sulphur of the ores would tend to counterbalance in some degree the disadvantages arising from the additional cost of freight or inland carriage in the case of works situate at a distance from Swansea or Liverpool. The Spanish and Irish (Wicklow county) pyrites contain from 1 to 4 per cent. of copper. The calcined residues are smelted with the addition of ⅛th of their weight of sand and ⅛th of poor uncalcined copper-ores. The regulus contains about 40 per cent. of copper. The slag is remarkably crystalline. As the regulus and slag are liable to be much intermixed, the assay of the bulk of the regulus seldom gives more than 12 per cent. of copper. (See note at the end of the article on copper).

Important practical conclusion concerning calcination.—The sulphur is only very imperfectly expelled, and more is left in the calcined ore than is sufficient to form disulphide of copper with the whole of the copper, and protosulphide of iron with an amount of iron equal in weight to that of the copper. The reader is, for the present, requested to fix his attention upon the four *essential* constituents of the ore, namely, *copper*, *iron*, *sulphur*, and *silica*: the changes which any other sulphides or other matters present in the ore may undergo will be separately considered hereafter.

2. *Melting of the calcined ore.*—The products are *coarse-metal* and *ore-furnace slag.*

External characters of coarse-metal.—It is brittle, and may easily be reduced to powder by trituration. The fractured surface of a piece of this metal is non-crystalline, uneven, more or less granular, generally vesicular, and bronze-like in colour.

Composition of coarse-metal.—Le Play made the following analysis of a sample, which was carefully prepared from a mixture of 58 specimens of coarse-metal taken at intervals during a fortnight from a furnace in which the nature of the charge was constant.

Copper	33·7
Iron	33·6
Nickel, cobalt, manganese	1·0
Tin	0·7
Arsenic	0·3
Sulphur	29·2
Slag, mechanically mixed	1·1
	99·6

Mr. Napier has published analyses of six specimens of coarse-metal, produced at different times in the ordinary process of smelting: they indicate considerable variation in composition. I have selected the two following, which contained respectively the minimum and maximum of copper.

	1.	2.
Copper	21·1	39·5
Iron	33·2	36·4
Sulphur	45·5	25·0
	99·8	100·9

Le Play proposes the formula $3\,Cu^2S + Fe^2S^3 + 4\,FeS$ as representing the composition of the coarse-metal produced in the Welsh method of smelting: the iron in the protosulphide is supposed to be partially replaced by other metals. But copper, iron, and sulphur may exist in very variable proportions in a regulus, which may, notwithstanding, be quite homogeneous throughout; and no evidence has been advanced to prove that coarse-metal should be regarded as a definite compound, and not as a mere mixture of two or more definite compounds. It is better that we should feel our ignorance than hastily apply formulæ on insufficient grounds to matters so variable in composition as a regulus of this kind.

External characters of ore-furnace slag.—It generally consists of a hard,

brittle, compact, opaque; black matrix, in which are imbedded sharply-defined angular pieces of white quartz, and hence it presents a porphyritic appearance. Its fracture is uneven, and may be here and there more or less vesicular. It frequently contains small shots of coarse-metal, which, on a freshly-broken surface, may be readily distinguished with the naked eye.

Composition of the ore-furnace slag.—Le Play determined the composition of a *sample* of this slag prepared from 58 specimens taken under exactly the same conditions as those from which the *sample* of coarse-metal was obtained. The results of his analysis are as follow:—

Quartz in admixture		30·5
Silica in combination		30·0
Alumina		2·9
Protoxide of iron		28·5
Lime		2·0
Magnesia		0·6
Various oxides (of tin, manganese, nickel, and cobalt)		1·4
Fluor	1·0	
Calcium	1·1	2·1
Copper	0·5	
Iron	0·9	2·0
Sulphur	0·6	
		100·0

The oxygen of the combined silica is nearly double that of the bases, so that in constitution this slag approximates to a sesquibasic silicate. According to Le Play this slag never contains the slightest trace either of oxide or dioxide of copper; and the copper which it contains exists only in the mechanically-diffused coarse-metal. The same author informs us, "that his numerous researches on this point led him to discover a fact which had previously escaped the attention of metallurgists, and which, in his view, constitutes the most general and essential characteristic of the theory of the smelting of sulphuretted ores of copper. This fact, which, without a single exception, is true of all the slags of the seven principal groups of copper-smelting works of Europe, may be enunciated as follows. If we analyze simultaneously the regulus and the slag produced at the same time in smelting sulphuretted ores of copper, we find that *for a given quantity of copper the slag always contains more sulphur than the regulus.* With the Welsh slag in particular I have established the following facts. The regulus produced during a fortnight in one of the furnaces (No. 2) contained on the average, copper 34·6 and sulphur 29·8. The slag produced at the same time, in the same furnace, contained on the average, copper 0·5 and sulphur 0·6. The proportion, therefore, of sulphur (for 1 of copper) is—

In the regulus	0·86 or 100
In the slag	1·20 ,, 140" [4]

The proportion of copper has been determined in our metallurgical laboratory in two specimens of ore-furnace slag from the Hafod Works: one contained 0·45 per cent., and the other 0·61 per cent. of copper.

[4] Op. cit., p. 212.

Le Play supposes that the excess of sulphur exists in combination with iron as protosulphide, which is "dissolved in the slag by the affinity of the silicate of protoxide of iron, forming a compound which might be called *sulphō-silicate* of iron. . . . The constant presence of the sulpho-silicate of iron in slags from the fusion of sulphuretted ores explains perfectly the absence of the oxides of copper, because the existence of these is incompatible with that of sulphide of iron. The oxide of copper, which at first tends to dissolve by the action of the silica, is reduced by the two elements of the sulphide. The metallic copper formed separates immediately from the slag, either to deposit itself or dissolve in the regulus."[5]

Simple inspection of ore-furnace slag suffices to prove that a sensible portion of the small quantity of copper which it contains exists in the state of coarse-metal, and, however probable it may be that the whole exists in that state, yet I do not find that Le Play has proved this to be the case. Moreover, he has neither demonstrated that the portion of sulphur which, in relation to the copper present, exceeds that contained in the coarse-metal, is in combination with iron, nor established the fact of the existence of such a compound as *sulpho-silicate of iron*. Admitting, for the sake of argument, that ore-furnace slag contains no oxide of copper, there would appear to be no difficulty in explaining the fact if we refer to the reaction between oxide of copper and sulphide of iron in the presence of silica, which has been previously described (see p. 254); for, supposing that some of the oxide of copper which was present in the calcined ore had combined with silica and passed into the slag, yet, as every part of this slag must have been thoroughly in contact with a large excess of sulphide of iron, as may be certainly inferred from the composition of the coarse-metal, any silicate of copper which it might have contained would have been decomposed with the formation of disulphide of copper and silicate of protoxide of iron. The necessity, therefore, of Le Play's hypothesis concerning sulpho-silicate of iron, under the circumstances, does not seem to be required. Le Play intimates that such a compound as sulpho-silicate of iron would afford but little interest to chemists;[6] but in this, I am inclined to think, he is mistaken. There is one very interesting mineral—helvin, or tetrahedral garnet—which has attracted much attention, because it consists of a silicate apparently in combination with a sulphide. It occurs well crystallized, and, according to Rammelsberg, has the following composition:[7]—

Sulphur	5·71
Silica	33·13
Glucina	11·46
Protoxide of manganese	49·12
Protoxide of iron	4·00
	103·42

The sulphur is believed to be in combination, partly with manganese and partly with iron, but whether in this mineral there is an

[5] Op. cit., p. 213. [6] Op. cit., p. 213.
[7] Handbuch der Mineralchemie, 1860, p. 700.

actual definite combination of a sulphide with a silicate is not yet proved on indisputable evidence. It is certain that many well-crystallized minerals do contain a considerable amount of matter—or "dirt," as it has been called—which is merely accidentally present, and is not an essential part of their constitution. Beautifully-crystallized slags of iron-smelting furnaces, as has been already remarked (p. 23), contain a small quantity of sulphide, which is certainly only mechanically diffused, because minerals identical in crystalline form and chemical composition, except that they contain no sulphide, occur in nature. In the sequel other instances will be given in which sulphides exist in small quantity in well-crystallized slags, which consist of definite silicates. It may be that it is an error to suppose that in these and other cases the sulphide is present in an uncombined state, but at least additional data are necessary to justify a positive conclusion on the subject of the existence of sulpho-silicates, notwithstanding the opinion of Le Play, that "the important function of the sulpho-silicate of iron throws new light on the metallurgy of copper."

Specific gravity of the coarse-metal and ore-furnace slag.—Le Play determined the specific gravity of these substances when in the state of fine powder. His results are as follow:—

Specific gravity of coarse-metal, containing 33·7 per cent. of copper..... 4·56
Do. slag, containing 1·5 of coarse-metal and 30·5 of quartz 3·21

Concluding observations.—From the preceding analytical data we learn that in the ore-furnace much of the iron and the whole of the so-called earthy matter of the ore are separated as slag, and that the whole of the copper, except the small quantity which escapes in the slag, is concentrated in a regulus, which contains, on an average, about as much copper as pure copper-pyrites. One portion of the quartz which existed in the ore combines with protoxide of iron, derived partly from the ore and partly from the *metal slag*, which is a silicate of protoxide of iron, containing a much larger quantity of this oxide than *ore-furnace slag*, while the remainder of the quartz is diffused through, and remains suspended in, the slag, because it has a lower specific gravity than either the regulus or the slag. The oxide of copper which is present in the calcined ore is entirely converted into disulphide, which passes into the regulus. This conversion is effected through the joint agency of sulphide of iron and silica, as has been previously explained. The oxide of iron in the calcined ore is in the two states of oxidation of protoxide and sesquioxide, and a considerable quantity of magnetic oxide may also be present. The metallic sulphides in the raw ore contain more sulphur than the *coarse-metal*. Sulphur must, therefore, be evolved during fusion in the ore-furnace. When any of the oxides of iron are heated in contact with excess of sulphur, sulphurous acid and protosulphide of iron are generated; but when either magnetic oxide or sesquioxide of iron is heated in contact with silica and a proportion of sulphur only just sufficient to combine with the oxygen in excess beyond what is required to form protoxide of iron, silicate of this oxide is obtained. Hence

it is easy to understand how the sesquioxide of iron in the calcined ore should be reduced to protoxide. It is observed, that during the fusion sulphurous acid escapes with effervescence from the melted mass. Any copper which may exist in the state of silicate in the *metal slag* forming part of the charge of the ore-furnace is converted into disulphide and passes into the *coarse-metal*; for when silicate of copper is heated with an excess of sulphide of iron, such as is always present in this furnace, silicate of protoxide of iron and disulphide of copper are formed. In like manner may be explained the extraction of copper from old fire-bricks, or other furnace residua impregnated with oxide of copper, when these are introduced into the ore-furnace.

3. *Calcination of the granulated coarse-metal.*—I have not met with a satisfactory analysis of this product. Le Play determined that the sulphur was reduced by calcination from 29·5 to 16·4 per cent. in *coarse-metal*, consisting of—

Copper	33·7
Iron	34·2
Various metals	1·5
Sulphur	29·5
Slag, mechanically mixed	1·1
	100·0

From the proportion of sulphur above stated he infers that the approximate composition of the product of the calcination of such *coarse-metal* is as follows :—

Copper	34·6	Coarse-metal, unchanged	54·9
Iron	35·1	Protoxide of copper	19·5
Various metals	1·5	Sesquioxide of iron	22·5
Sulphur	16·4	Various oxides	2·0
Oxygen	11·3		
Slag, mechanically mixed	1·1	Slag, mechanically mixed	1·1
	100·0		100·0

Le Play does not appear to have analysed this product, and it is not possible, from the determination of the sulphur alone, to deduce its composition. It may, indeed, be regarded as certain that the composition assigned cannot be correct; for, so long as a considerable amount of the *coarse-metal* remains unchanged, the oxides of copper and iron could not have wholly existed in the high degrees of oxidation supposed.

According to Mr. Napier "the following analyses give a fair average of the results of calcining *coarse-metal*."

	Before calcination.	After calcination.
Copper	32	33
Iron	36	36
Sulphur	25	13
Oxygen	...	11
Insoluble matter	7	7
	100	100

Rough results of this kind will hardly satisfy an analyst of the present day, any more than the preceding deductions of Le Play. They

may be correct, or, as is probable, they may not. It is, however, certain, that during calcination a considerable amount of sulphur is evolved in the states both of sulphurous and sulphuric acids.

4, *Melting of calcined granulated coarse-metal.*—The composition of the regulus produced in this operation will vary with the proportion of oxide of copper in the matters which are fused in conjunction with the calcined granulated coarse-metal. It is only when a sufficient quantity of ore containing oxide of copper, such as the Australian carbonates and red oxide, is added along with the *roaster* and *refinery* slags, that the regulus occurs in the state of *white-metal.*

White-metal.—It is compact and brittle. Its fracture is uneven, granular, and more or less crystalline; it has a feebly metallic lustre and dark bluish-grey colour.

Le Play has given the following analysis of a characteristic specimen of this *metal*:—

Copper	77·4
Iron	0 7
Nickel, cobalt, manganese	traces
Tin, arsenic	0·1
Sulphur	21·0
Slag and sand, mechanically mixed	0·3
	99·5

It was selected from a part most free from cavities, and had a specific gravity of 5·70. Le Play found that an average sample, prepared from numerous varieties of *white-metal* collected during a fortnight, contained 73·2 per cent. of copper. From the preceding analysis it appears that *white-metal* approximates closely in composition to disulphide of copper. The proportion of sulphur, however, after deducting the maximum amount which may be combined with the iron and other metals, is sensibly greater than that in disulphide, but possibly to this extent the analysis may be erroneous.

Slag.—This slag resembles some of the slags produced in the manufacture of iron. It is brittle, compact, and occasionally very crystalline. Its fracture has the following characters:—uneven, more or less conchoidal, granular, or distinctly crystalline; here and there, especially towards the upper surface, it presents small rounded cavities, caused evidently by gas; its colour, when freshly fractured, is dark bluish-grey; in parts it appears somewhat iridescent, the tints ranging from blue-grey to bronze-yellow; its lustre inclines to metallic; in places, especially near the button, small round shots of regulus may be observed, which may be readily distinguished from the surrounding slag by their lighter bluish-grey colour and more highly metallic lustre. The following analysis is by Le Play:—

Silica	33·8	Magnesia			0·3
Alumina	1·5	Slag, mechanically mixed	Copper	2·9	
Protoxide of iron	56·0		Iron	0·3	
Dioxide of copper	0·9		Sulphur	0·8	
Various oxides	2·1				
Lime	1·4				100·0

Le Play states, that in what he terms rich slag the dioxide of copper amounts to 2·7 per cent. A specimen of *metal-slag* which I procured from the Hafod Works contained not more than 1·83 per cent. of copper.

White-metal may be regarded as *coarse-metal* deprived of nearly the whole of its sulphide of iron. The same result would have been directly attained by heating together *coarse-metal*, oxide of copper, and silica, intimately mixed in such proportions that the oxygen of the oxide of copper should just be sufficient to convert the iron of the *coarse-metal* into protoxide, and the silica sufficient to combine with the protoxide thus formed and produce an easily-fusible slag. The following formulæ exactly express the reactions:—

$$FeS + Cu^2O + xSiO^3 = Cu^2S + FeO,xSiO^3$$
$$2FeS + 2CuO + xSiO^3 = Cu^2S + S + 2FeO,xSiO^3.$$

By the calcination of the *granulated coarse-metal* a certain amount of sulphur has been evolved and replaced by an equivalent proportion of oxygen, or, in other words, a product has been obtained consisting essentially of copper, iron, sulphur, and oxygen. Oxide of copper (Cu^2O and CuO) has also been added by introducing into the furnace *roaster* and *refinery* slags and ores containing carbonate of copper. But the *calcined granulated coarse-metal*, the two slags above-mentioned, and, probably, the ore, contained oxide of iron. The presence of this oxide does not affect the result. The oxide of iron in the slags is already in combination with silica, and continues so; and if we refer to the analysis of the *calcined granulated coarse-metal*, we shall find that there remains more sulphur than is sufficient to form disulphide of copper with the copper present and to combine with the excess of oxygen beyond what is required to form protoxide of iron with the iron present, so that there is no difficulty in understanding how any sesquioxide of iron should be reduced to protoxide. We have only, therefore, to fix our attention on the proportions of copper, iron, sulphur, and oxygen, which may exist in the various matters introduced into the furnace, quite irrespective of the manner in which these elements may be combined with each other, in order to have a clear comprehension of the metallurgical reactions which concur in the production of *white-metal*. The silica required to combine with the protoxide of iron may be derived, not only from the slags added, but also from the ore and materials of which the furnace is made.

On the large scale it would not be desirable, even were it practicable, to effect an intimate mixture, in the manner supposed, of the various matters composing the charge. Such a course would, on the ground of expense alone, be inexpedient, and would, it is alleged, be disadvantageous in other respects. In the first place it is stated that the bottom of the furnace would be exposed for a considerable time to contact with the oxides of copper and iron, and would, consequently, be much corroded, whereas, by the present system, the unchanged regulus remaining in the *calcined granulated coarse-metal* fuses rapidly and trickles down on the sand bottom of the furnace, which is thereby protected from such corrosive action; and, in the second place, me-

tallic copper would be liable to be separated, which, in the present stage of the process of smelting, should be avoided, because copper thus reduced would, for reasons to be hereafter explained (see *best selected process*), be very impure.[8] But this result would also occur in the usual method of conducting the fusion if a considerable excess of oxide of copper should happen to be put into the furnace. Le Play defers to the judgment of workmen on questions of this nature to a much greater extent than many experienced smelters in this country would, I think, be disposed to do.

In the first stage of this operation a regulus is formed which contains much less copper than *white-metal*, and a considerable time is required completely to liquefy the matter with which its surface is, in a greater or less degree, covered. This matter is, as we have seen, rich in oxide of copper, much of which is combined with silica. A gradual interchange takes place between the elements of this silicate of copper and those of the sulphide of iron in the regulus, whereby the latter becomes enriched with the addition of disulphide of copper, of which the copper is derived from the superincumbent slag and ore, and in a corresponding degree deprived of sulphide of iron. Le Play makes the following remarks:—"The oxide of copper especially acts upon the sulphides of iron and copper, producing metallic copper, protoxide of iron, and sulphurous acid. The undecomposed sulphides not being completely saturated with metals dissolve the copper."[9] Now the only sulphides to which he can refer are disulphide of copper and protosulphide of iron, but I am not aware that either separately has the power of dissolving metallic copper, though when combined they may possess that power in a limited degree.

It is not to be supposed that the proportions of the various matters which form the charge of the furnace in this operation can always be so nicely adjusted as to produce a regulus so nearly approximating to the composition of disulphide of copper as the specimen of *white-metal* of which the analysis has been given. Should the oxidized compounds of copper be deficient, as from the exhaustion of the stock of ores containing carbonates and oxide of copper, the regulus would contain a considerable quantity of iron, and constitute what, in consequence of its bluish colour, is termed *blue-metal*. On the other hand, should these compounds be in excess, some copper would be reduced, and a regulus obtained similar in composition, colour, and fracture to *white-metal*, but when cold presenting on its upper surface numerous small, round, pimple-like excrescences, which have caused it to be termed *pimple-metal*. *White-metal* passes insensibly into *blue-metal* as the proportion of iron increases, and between the two there is no line of demarcation.

Blue-metal.—It is brittle and breaks with an uneven fracture. The colour of its fractured surface is modified by the temperature at which it is produced. When broken hot, but much below a red-heat, it has a fine, deep, purplish-blue colour; but when broken cold, it has a pur-

[8] Le Play, Op. cit., p. 250. [9] Op. cit., p. 256.

plish-red bronzy tint, of which it is difficult to convey an accurate notion by description: its lustre strongly inclines to metallic. On examining the freshly-fractured surface of a characteristic specimen, from which the preceding description was taken, under a good lens, it is seen to be studded throughout with bright, metallic, copper-like particles, and the peculiar colour and lustre which it possesses seem to result from the combined effect of these particles and the purplish-blue matrix of regulus in which they are embedded.

Le Play has given the following analysis of a sample prepared from a mixture of all the varieties of *blue-metal* produced during the course of a week in the same furnace:—

Copper	56·7
Iron	16·3
Nickel, with traces of manganese	1·6
Tin, with traces of arsenic	1·2
Sulphur	23·0
Slag, mechanically mixed	0·5
	99·3

Of several analyses of *blue-metal* published by Mr. Napier, one is nearly the same as this of Le Play.

Slag.—There is nothing characteristic in the slag which may be formed in conjunction with *blue-metal;* it may be regarded as in all respects similar to that of *white-metal*, of which an analysis has been already presented. It may be expected to contain less copper in the state of oxide in proportion as the regulus is rich in iron.

In the preceding analysis the amount of sulphur required to form disulphide of copper and protosulphide of iron with the copper and iron present is 23·64, so that there is a deficiency of 0·64 in addition to that needed for the various metals which must have existed as sulphides. This deficiency would be readily explained by the fact that metallic copper is generally present in *blue-metal.* The copper is diffused through the mass in minute angular particles, *not in the least globular like shot*, and, for the most part, invisible without the aid of a good lens; and where cavities occur, it may be seen protruding into the interior in the form of teeth and delicate hair-like filaments. Le Play has well described these appearances.[1]

Now, as Le Play has remarked, it appears singular that metallic copper should occur as the rule in *blue-metal* and only as the exception in *white-metal*, notwithstanding *blue-metal* is necessarily the intermediate stage between *coarse-metal* and *white-metal*, and no metallic copper is separated in the furnace until the operation following the fusion in which *white-metal* is produced. One might be disposed to infer that, if copper existed in a free state in *blue-metal, à fortiori* it should exist, even in greater proportion, in *white-metal.* If free copper had been present in the liquid regulus in the furnace, so far as my knowledge extends, there is every reason to suppose that it would have assumed the form of globules, and subsided, in a greater or less degree, on the bottom of

[1] Op. cit., p. 272.

the furnace. On the other hand it is difficult to understand how the copper, which is seen to be free in a piece of solid regulus, should have existed in a state of combination in the liquid regulus, because the amount of sulphur found by analysis does not suffice to convert the copper into disulphide and the iron into protosulphide. But the following fact, recorded by Plattner, tends to remove this difficulty. Copper regulus of a bluish-black colour, and consisting of $x\mathrm{Cu^2S}+\mathrm{FeS}$, may, during fusion, take up a small additional quantity of metallic copper, which, on the subsequent rapid solidification of the regulus, does not separate; a grey colour is thereby communicated to the finely-granular fractured surface of the regulus. When the regulus thus enriched with copper is melted and allowed to cool slowly in a crucible, its fractured surface will regain its original bluish-black colour, and present, here and there, small cavities lined with little teeth of metallic copper. According to Plattner this effect is due to the action of protosulphide of iron (FeS), which, during the melting of the regulus, yields a portion of its sulphur to the metallic copper, forming disulphide of copper and disulphide of iron ($\mathrm{Fe^2S}$). When this disulphide of iron is kept fused at a certain temperature, and afterwards rapidly solidified, it undergoes no change; but when, on the contrary, it is allowed to cool slowly after fusion, owing to the affinity of disulphide of copper for protosulphide of iron, the disulphide of iron is again converted into protosulphide at the expense of the sulphur of some of the disulphide of copper, with the separation of an equivalent proportion of metallic copper. During the process of cooling the regulus contracts considerably, and, as solidification proceeds from without inwards, cavities are formed, into which the liberated copper protrudes. These internal cavities are due less to the escape of gases or vapours than to the cause just assigned.[2]

A somewhat analogous play of affinity at different temperatures seems to occur between the oxides of copper and iron when in combination with silica. I have a specimen of glass (silicate of soda and lime) which contains both copper and iron, and has a pale green colour. When this glass is heated to the degree at which it softens or melts, and is afterwards *rapidly* cooled, its colour is not changed; when, on the contrary, after having been thus heated it is *slowly* cooled, or, after having become cold, it is gently reheated, it acquires an intense red colour like that communicated to glass by dioxide of copper. The glass which has become red regains its original green colour by being strongly reheated and afterwards rapidly cooled. This alternation of colour may be effected any number of times. The experiment may be easily made by heating the glass before the blowpipe beyond the point of the flame; and, as far as I have observed, the phenomenon is independent of any oxidizing or reducing action from without. Dioxide of copper has a much greater colouring power than an equivalent proportion of protoxide, for glass of which the surface contains protoxide of copper sufficient merely to communicate a just perceptible greenish-

[2] Berg. u. Hüttenm. Zeitung, 1855, p. 143.

blue tinge becomes intensely red by being heated in a reducing gas. The alternation of colour above described may be susceptible of the following explanation. At a high temperature only protoxide of copper, in association with some protoxide of iron, exists; but at a low temperature it is reduced to dioxide, with the formation of an equivalent proportion of sesquioxide of iron, which has but a feebly colouring power as compared with protoxide of iron.

I have made the following experiments with a view to ascertain the conditions under which the separation of metallic copper occurs in *blue-metal*.

1. A characteristic specimen of *blue-metal*, through the substance of which metallic copper was diffused in fine particles, was melted under charcoal in a very small covered clay crucible at a bright red-heat, and the crucible, immediately after its removal from the furnace, was plunged into cold water, so that the melted regulus might be cooled with the utmost rapidity. By the action of the water some sulphuretted hydrogen was evolved. The regulus had been thoroughly fused. On the surface of the button which had been in contact with the crucible numerous circular cavities existed, due clearly to bubbles of gas. The prevailing colour of this surface was dull copper-red, which was produced by extremely minute particles, or, as it were, dust of copper, for the characteristic metallic lustre and colour of copper were instantly developed by drawing the end of a penknife over a portion of the red surface. On holding the regulus obliquely towards the eye, the red deposit of copper presented a velvety aspect. The button was friable, breaking easily in the direction of cracks, which appear to have been caused by the rapid cooling in water. The fracture was uneven, and more or less conchoidal. There were a few tolerably large globular cavities towards the exterior, but the mass was generally compact, except in the central portion, where the fracture was hackly, as though small spaces had been produced by contraction during solidification. The red copper dust was visible to the naked eye to a greater or less extent over the entire fractured surface, but it was most abundant towards the exterior. On looking at the surfaces of some fragments placed at *right angles* to the line of vision, the colour was dark bluish-grey, with a distinct vitreous lustre; but on looking at the surfaces of the same fragments placed *obliquely* before the eye, the copper-red colour became more or less evident. I examined various fragments under a simple microscope, and observed copper-like particles where I could detect none with the naked eye.

2. Another piece of the same *blue-metal* was melted under charcoal in a very small covered clay crucible at a bright red-heat, and the crucible was left to cool in the air. The regulus was perfectly melted. On the external surface, which had been in contact with the crucible, were numerous small globular cavities, which had evidently been caused by bubbles of gas: many of these, which were disclosed by detaching the adherent particles of crucible, were completely coated internally with filaments of copper, directed towards the centre; others contained only a few minute projecting teeth of copper; and

others, again, were free from copper. The outer portion of some of these cavities was formed by the substance of the crucible. The cavities lined with copper were beautiful objects under a simple microscope. The prevailing colour of the whole surface, except the top of the button, was dark bluish-grey, intermixed with red. The red was less intense, and was due to particles of metallic copper, larger and more distinct than in the first experiment. The top of the button was dull, and was covered with small, angular, apparently-crystalline, isolated, and slightly projecting particles of copper. The regulus was very much less friable than that which had been cooled in water. The fracture was tolerably even; less conchoidal and vitreous than that of the button in Exp. 1; its colour was dark purplish-grey with a reddish hue. The tint changes somewhat with the direction in which the surface is seen; under a lens, or simple microscope, minute angular particles like metallic copper were observed, apparently equally distributed over the whole surface.

3. Another portion of the same *blue-metal* was melted in a covered clay crucible, placed in another crucible and surrounded with anthracite powder. Fusion was effected at a bright red-heat, and the whole left to cool in the furnace until the following morning. The button was well melted. The top was concave and dull, and, under a good lens, no particles of metallic copper could be detected upon it. The remaining surface of the button, which had been in contact with the crucible, presented nearly the same appearances as in Exp. 2. There were several small globular cavities lined with protruding fibres of copper. The fracture was similar to that of the button in Exp. 2, except that it had a dark bluish-grey colour without the decided red tinge which the other possessed. When the two were compared side by side, the difference of tint was very decided. On examining the fracture under a simple microscope, minute angular particles, like copper, were observed in every part.

4. Disulphide of copper, prepared by heating *best-selected copper* and sulphur together and fusing, was intimately mixed by trituration with a sulphide of iron[3] containing 29·9 per cent. of sulphur, and prepared by heating thin sheet-iron and sulphur together. The proportions were as 7 to 3. Of this mixture 600 grains were triturated with 120 of the powder of copper (obtained by reducing oxide of copper in a current of hydrogen), and heated to bright redness in a covered clay crucible contained within another covered crucible, the space between the two being entirely filled with anthracite powder so as to cover the top of the inner crucible. The button was well melted. The external surface was studded with globular depressions or cavities, some very small and others as large as an ordinary pin's head, most of which were filled with converging filaments of copper. On the fractured surface small angular particles, or small laminæ of metallic copper, appeared throughout; but the central portion, in which spaces seemed to have been caused by contraction during solidification, consisted

[3] It contained 6·46 per cent. less sulphur than true protosulphide of iron.

apparently of a crystallized regulus mixed with so much fibrous copper as to communicate a coppery-red colour to the whole of this portion. Under a simple microscope this mixture of crystals of regulus and fibres of copper was extremely interesting. In no part did I detect any shots of copper, not even at the bottom of the button.

5. Exp. 4 was repeated with 500 grains of the mixture triturated with 50 of the powder of copper. The regulus was well melted. The fractured surface was beautifully mottled with coppery-red and bluish-grey. Under a lens or simple microscope, minute, angular, copper-like particles were everywhere observed on the fractured surface. The external surface of the button presented similar characters to that of Exp. 4. I did not detect any shots of copper in any part of the button, not even at the bottom.

6. Exp. 4 was repeated with 500 grains of the mixture without the addition of metallic copper. The product was well melted. The characters of its outer surface and fracture were in all respects similar to those of the last, and, as far as the eye could enable me to judge, the amount of metallic copper diffused seemed to be quite as great as that in Exp. 5.

7. A mixture consisting of 250 grains of the mixture employed in Exp. 4 and 250 grains of disulphide of copper was heated in a clay crucible enclosed in another containing anthracite powder. The button was well melted. The outer surface of the button, except the top, was studded with small globular concretions of fibres of copper, which appear to have been deposited in the interior of cavities. These copper-lined cavities, or concretions, as I observed in buttons which have been previously described, are much more numerous round the sides of the button. At the bottom of the button were numerous small globular cavities, which were either empty or contained only a few protruding teeth of copper. The fracture was uneven, and in places conchoidal. It was beautifully mottled with fine-bluish purple and rich coppery-bronze, and was everywhere studded with minute, angular, copper-like particles. No shots of metallic copper were found.

8. The mixture used in Exp. 4 was triturated with a large excess of sulphur, and heated simply in a covered clay crucible in a muffle to bright redness, without being protected by charcoal or anthracite powder. The product was well melted. On the surface were numerous globular cavities, but in none did I observe any metallic copper. The fracture was uneven; it had a reddish bronze-like colour, mottled with dark-purplish grey, with metallic lustre; there was one considerable cavity near the centre, which was lined with distinctly crystallized dark-grey regulus. The mass seemed to consist of a mixture of two kinds of regulus, distinguished by the colours above mentioned. With the naked eye or even under a common lens I could not detect the presence of metallic copper; but under a simple microscope the whole mass seemed, as it were, infiltrated with copper in very fine particles. The bronze-like colour is evidently due to copper thus finely disseminated.

9. A mixture consisting of 300 grains of disulphide of copper and

136 of iron-pyrites, from South Wheal-Frances, was heated in the same manner as the mixture in Exp. 4. The product was well melted. No metallic copper could be observed on the surface. The fracture was uneven; its colour was coppery-bronze, resembling that of the button in Exp. 8, but richer, and with a more highly metallic lustre; in places this fine colour was uniform, but for the most part the surface was mottled with a mixture of this colour and dark-bluish grey. Under a simple microscope minute particles of copper were seen to be diffused everywhere through the mass, and thus examined it was evident that the rich bronze colour was entirely caused by particles of metallic copper, just as in the last experiment.

10. Some of the disulphide employed in the foregoing experiments was heated *per se* in a covered clay crucible, enclosed in another crucible containing anthracite powder, just as in Exp. 4. The product was well melted. The fracture was somewhat uneven and conchoidal. There were cavities on the outer surface, as well as a few in the interior, in all of which were observed angular, apparently crystallized, isolated copper-like particles.

11. Some of the same disulphide was mixed with a large excess of sulphur, and heated just as in the last experiment. The button was perfectly melted. Angular metallic particles were observed on the top, as well as the sides of the button, which had been in contact with the crucible. The fracture was even, smooth, almost vitreous in lustre, and somewhat conchoidal; the colour was dark grey, like that of disulphide of copper; a single cavity existed on the fractured surface, in which angular particles of metallic copper were observed, but on no other part of the surface could a speck of copper be detected.

12. A mixture of 500 grains of disulphide of copper in powder and 100 of copper turnings was exposed in a covered clay crucible to a strong heat in a muffle during about two hours. The crucible was then taken out, cooled as rapidly as possible, and broken. At the bottom was a button of copper weighing 68 grains. No metallic copper was detected in the disulphide, which had the usual appearance, and was not in the least crystallized.

13. The last experiment was repeated, and the crucible left in the muffle during the night to cool. A button of copper, weighing 77 grains, was found at the bottom. Here and there on the surface of the button particles of copper were observed, but not in the form of moss; and the top was covered with small crater-like prominences, as though produced by the evolution of gaseous matter; the fracture of the disulphide was crystalline.

14. Feathered shot copper, *best-selected*, was melted with a large excess of roll-sulphur in a Cornish crucible. The whole was well stirred with a piece of wood, then covered with charcoal, and left to cool slowly in the crucible out of the furnace: particular care was taken to exclude the presence of iron. When perfectly cold, a well-melted lump of disulphide of copper was detached from the crucible, 3 inches in diameter at the top and $2\frac{1}{2}$ deep in the centre; it weighed 12.710 grains, inclusive of a button of copper at the bottom weighing

775 grains. The lump was broken nearly vertically through the middle, when several cavities were disclosed, which measured from $\frac{1}{4}$ to $\frac{3}{4}$ inch in diameter, and were mostly in the upper half of the fractured surface; there were other and smaller cavities. In several of these cavities, large as well as small, were projecting teeth and filaments of copper; but I did not observe particles of copper anywhere imbedded in the mass. The surface produced by a fresh fracture had the characteristic dark bluish grey colour of disulphide of copper; but, after exposure to the air, it acquired here and there a rich blue tarnish. The copper in the button at the bottom was brittle, somewhat vesicular, and of a greyish red colour, very similar to that which appeared on the fractured surfaces of some of the specimens of regulus obtained in the preceding experiments.

The last three experiments would seem to indicate that disulphide of copper alone may possess the property of taking up during fusion a small quantity of copper, which is again set free during solidification; but, inasmuch as there was no uniform diffusion of copper in minute particles through the mass, and as the copper which was disclosed on fracture was very small in amount and confined entirely to the cavities which existed, the evidence is not sufficient to justify a positive conclusion on the subject. The presence of copper in these cavities may have depended upon the action of the gaseous matter which caused their formation. What this matter was, and how it came to be present, I have as yet no certain knowledge.

To account for the presence of metallic copper in *blue-metal*, Le Play has propounded a theory which, he asserts, "explains all the special facts of the Welsh method (of smelting), and which, moreover, throws great light upon a multitude of operations peculiar to the copper-smelting works of the continent of Europe."[4] It is obvious from this language that he regards this theory as highly original and important. That there may be no mis-statement on the subject, I subjoin a literal translation of Le Play's description of it, and the evidence on which it is founded:—

"Metallic copper, the presence of which characterizes *blue* and *red-metal*,[5] is not actually deposited during fusion; it is a product which is only formed after the matters have left the furnace. When, after tapping, the regulus and slag are superposed in the mould destined to receive them, these two substances continue during some time to act upon each other as they did in the interior of the furnace, and to make an exchange of the two metals (copper and iron). But affinities are gradually modified by the progressive cooling of the two reacting substances. A moment arrives when the temperature of the regulus, still perfectly fluid, falls to that at which copper tends to assume the solid state; from this moment the reaction, which before was simple,

[4] Op. cit., p. 273.

[5] This term is applied by some smelters to a regulus less advanced than *blue-metal*, that is, one containing more iron than the latter, and less than *coarse-metal*. The red colour is due to dispersed minute particles of metallic copper.

becomes double;[6] the iron of the regulus combines with the oxygen of the dioxide of copper; but the copper set at liberty, instead of combining with the sulphur previously combined with the iron, is in some way deposited in the molecular state, the temperature not being sufficiently high either to compel the copper to combine with the regulus, or to cause it to collect in distinctly melted globules. The phenomenon takes place, then, during that period of the cooling of the matters tapped out when the regulus and slag still preserve the fluid state at their surface of contact, and while the temperature of the regulus already borders on that at which copper solidifies."

The arguments adduced by Le Play in support of this theory are the following:—

1. If metallic copper had existed in *blue* or *red* metal before tapping, it is not conceivable that at the white heat which prevails in the furnace the metal should preserve the pulverulent or filiform state in which it is found in the cooled regulus, and not subside to the bottom.

2. When, according to Le Play, a furnace containing *blue-metal* is tapped, so that one portion may flow into a mould apart and free from admixture of slag, while the remainder is allowed to take its usual course and to solidify under the slag, copper is always entirely absent from the former, but is present in large quantity in the latter.

3. Le Play having remarked that *blue-metals*, identical in external characters, became charged with very unequal proportions of metallic copper, suspected that this might be due to a variation in the proportion of dioxide of copper dissolved in the silicate. Admitting the correctness of his theory, it should follow that in a regulus containing the same amount of sulphide of iron, the metallic copper ought to be proportionate to the dioxide of copper in the slag. This conjecture was subsequently confirmed by analysis.

4. It occurred to Le Play that he might be able to determine at will the production of metallic copper in any particular part of the regulus after tapping, either by introducing sulphide of iron into a *very white metal*, or dioxide of copper into a slag which contained but little of that oxide. He often made experiments of this kind, which always responded to his expectation.

5. In the middle of the bed destined to receive the contents of the furnace, Le Play made a circular cavity 0^m 60 (23·6 in.) in diameter, and 0^m 25 (9·8 in.) deep in the centre, towards which the sides sloped gradually down. This cavity, which was in communication with the rest of the bed, became completely filled with regulus, and then covered with a mass of slag 0^m 25 (9·8 in.) thick. As soon as the tapping was over, he introduced at one spot into the regulus, according to the nature of the matters upon which he was operating, a more or less strong dose of very ferruginous *coarse-metal*, and an equivalent dose of silicate of dioxide of copper into the corresponding part of the slag. Immediately after the pellicle of slag on the upper surface had solidified, charcoal powder

[6] "Dès ce moment la réaction devient simple de double qu'elle était."

and a considerable mass of sand were projected upon it, so as to prevent sudden cooling. In one experiment of this kind, at the junction of the regulus and slag, was found a large geode, of the capacity at least of 200 cubic centimetres (30·4 cub. in.), and entirely filled with extremely delicate threads of metallic copper, iridescent with the most vivid colours, and possessing nearly the same degree of flexibility as threads of organic matter. The whole of this deposit had about the same consistency as a large mass of tow. The copper thus separated had the following composition :—

Copper (by dry assay)	98·2
Iron	0·4
Nickel	0·6
Intermixed sand and carbon	0·2
	99·4

I shall now proceed to consider the proofs of the theory in question *seriatim*. 1. It is a fact that *blue-metal*, richly impregnated with metallic copper, may be re-melted at a high temperature, without causing the copper to subside and collect in mass at the bottom. The experiments recorded at pp. 352, 3, establish this fact beyond question. 2. Issue must here be joined with Le Play on a point of observation. Metallic copper is not absent from *blue-metal* which has solidified without a covering of slag. I have it on the authority of an acute and experienced smelter, that *blue-metal* may be tapped out of the furnace without any admixture of slag, and yet contain metallic copper disseminated through its mass. Again: if a large mass of *blue-metal* be carefully examined under a microscope, metallic copper may be seen disseminated, apparently in isolated particles, and in equal quantity throughout. Now, if this separation of metallic copper were effected at the junction of the regulus and slag, it might certainly be expected to exist to a much greater amount in the vicinity of this junction; and it might be supposed that fibres of copper more or less continuous would be traceable in the regulus from the upper surface, descending in a vertical direction; which is not the case. 3. The argument concerning the connexion between the varying proportion of dioxide of copper in the slag and the proportion of metallic copper in the regulus is not of much weight; because this proportion may, nay, doubtless does, depend on that of the sulphide of iron in the regulus; and a relation must necessarily exist between this proportion of sulphide of iron and that of the dioxide of copper in the slag. Hence an effect which Le Play directly ascribes to the proportion of dioxide of copper in the slag, may be entirely due to the proportion of sulphide of iron in the regulus, *of which that of the dioxide in the slag is the measure*. 4. The experiment concerning the addition of sulphide of iron *to very white metal* furnishes no proof in favour of Le Play's theory of the supposed action of the oxide of copper in the slag; because metallic copper is separated by the addition of sulphide of iron to disulphide of copper when no slag is present. It seems rather difficult to understand how a satisfactory result should be obtained by adding dioxide of copper,

or matters containing it, to the slag after its removal from the furnace, unless it be at a very high temperature and extremely liquid. But if this had been the case in Le Play's experiment, the copper separated ought certainly, according to his own views, to have been well melted and deposited in the state of shots. 5. That filamentous copper may be formed without the agency of silicate of dioxide of copper, may be inferred from the fact that cavities in *every part* of pigs of *pimple-metal* may be full of it; and I am informed by Mr. William Edmond, that it may even be seen exuding *from under the pigs into the sand beds.*

From a review of the evidence which has now been presented concerning the presence of metallic copper in *blue-metal*, it appears to me that while the theory of Le Play cannot be maintained, the theory of Plattner is supported by strong evidence, both of observation and experiment. Indeed, when the fractured surfaces of *blue-metal* and of some of the specimens of regulus obtained in the preceding experiment are carefully examined under a microscope, it seems difficult to resist the conclusion that the liberation of metallic copper must have been due to *a cause operating equally through the mass.* In some cases the copper is diffused in particles so numerous and minute as to be quite imperceptible to the naked eye, when it produces a reddish-brown uniform colour. Admitting that such an equally acting cause does operate through the mass of the regulus during the process of cooling, as the theory of Plattner requires, all the varied appearances which have been described may be perfectly explained. The copper is liberated during solidification,—according to my experience, whether slowly or rapidly effected,—and may be re-dissolved on subsequent fusion The separation of carbon in the form of graphite during the solidification of grey-pig iron may be adduced in illustration of the separation of copper in *blue-metal.* That graphite exists diffused through solid grey-pig iron will be shown hereafter. When the iron re-melted, the graphite must dissolve in the liquid metal; for otherwise, on account of the great difference in specific gravity between it and the iron, it would necessarily rise to the top, which is not the case.

Moss-copper.—In copper-works this term is commonly used to designate those accumulations of filamentous, or moss-like copper, which are formed in cavities in pigs of certain kinds of regulus. Mr. Edmond informs me that, in making copper from Cornish ores, moss-copper seldom appears; but more of it is produced when these ores are melted in admixture with a little Irish ore (copper-pyrites mixed with *much iron-pyrites* ?): it occurs most abundantly when foreign ores are much used. It is chiefly observed and in the finest state in *pimple-metal*, when all the cavities are filled with it, and it is found protruding from the bottom of the pigs into the sand underneath; sometimes a little of it, strong and wiry to the touch, appears on the upper surface of the pigs. According to Mr. Edmond, it may be seen in the little prills, or shots of *metal*, in the *ore-slag;* and the surfaces of the pigs of metal from the *calcined-metal* furnaces are covered with a coating of it, generally of a dark colour, and as thick as the nap, or pile, on velvet. In specimens in my collection the filaments of copper vary in size

from the finest thread to fibres $\frac{3}{10}$ of an inch in diameter; and from one of these specimens, obtained by Mr. Edmond from a *fine-metal* furnace bottom, I have taken separate filaments perfectly continuous, and exceeding five inches in length. Under the microscope, the filaments present numerous minute, parallel, and longitudinal lines, or grooves, as though they consisted of bundles of extremely delicate fibres. Sometimes a continuous stratum of copper is found, entirely composed of densely-packed, delicate, parallel fibres. A remarkable specimen of this kind has been presented to me by Mr. Edmond, who obtained it from a *roaster-furnace* bottom. The stratum is $\frac{5}{8}$ of an inch thick in the thickest part, and appears to have been formed in a narrow flat cavity in dark grey regulus, from the opposite walls of which the fibres seem to have been protruded until they met: the supposed plane of junction of the ends of these fibres is indicated by a layer about $\frac{1}{16}$ of an inch thick, of a rich ruby colour, like that of the surface of Japan copper; and along this plane the fibres are more or less contorted and convoluted. The colour of the fibres, even in the same mass, varies from brass-yellow to ruby-red; and occasionally it is pale grey, like that of slightly-tarnished silver: it is due to superficial tarnish by oxidation, or otherwise.

The mode in which these fibres are produced is an interesting subject of inquiry. Each fibre seems to have been pushed, as it were, through a draw-plate, and at a temperature when the metal was soft, but certainly not exceeding that of well-melted copper; for otherwise the fibres, immediately after their protrusion, would have been re-melted into globules. Filaments of silver, which, examined under the microscope, appear to possess *identically the same structure* as those of moss-copper, may be formed by heating finely-divided sulphide of silver in a current of hydrogen at a temperature sufficient to agglutinate the sulphide, but below the actual melting-point of silver. This beautiful experiment may be made in a glass-tube, through which a current of the gas is passed. Long delicate fibres of silver may be seen protruding from minute rounded masses of the sulphide; and as they are produced while these masses are in a soft state and lying free in the tube, the idea that they result from the application of external mechanical pressure, in a similar manner to maccaroni, can hardly be entertained. There seems to be a force in operation at the base of each filament, which causes the particles of silver at the moment of liberation successively to arrange themselves in one continuous fibre, or series of fibres; or in other words, each filament grows, as it were, from a root imbedded in sulphide of silver.

Moss-copper is said to be remarkable for its purity, and to be equally pure whether the blue-metal on which it occurs may have been produced from the purest or most impure ores.[7] At p. 358 an analysis by Le Play of moss-copper has been recorded.

The following analyses of this substance are given by Mr. Napier:—

[7] Napier, op. cit., v. p. 346.

	1.	2.
Copper	98·5	99·0
Sulphur	0·4	0·4
Tin, Antimony, etc.	1·0	0·5
Iron	trace	trace
	99·9	99·9

No. 1 was brass-yellow in colour, and No. 2 red.

Now, if the copper forming moss-copper had been set free at a temperature above the melting-point of copper, it would, in subsiding through the bath of regulus, have reduced, more or less completely, any sulphide of tin or antimony with which it might have come in contact; and *copper-bottoms*, consisting of very impure copper, would have been obtained.

Blue-metal is converted into *white-metal* by melting it in contact with slags rich in silicate of dioxide of copper, or ores containing carbonate or oxide of copper and silica; and at first it might seem difficult to understand how this conversion should be effected by the agency of *oxidized* compounds of copper, as *blue-metal* contains disulphide of copper and metallic copper, whilst *white-metal* may be practically regarded as pure disulphide. Whether Plattner's theory of the existence and *modus operandi* of disulphide of iron be true or not, if we admit his statement that a certain regulus, consisting of copper, iron, and sulphur in the proportions requisite to form disulphide of copper and protosulphide of iron, has the power of dissolving some metallic copper, the difficulty just alluded to may easily be removed. Thus, suppose we have a regulus, of which the composition may be represented by the empirical formula $x\mathrm{Cu^2S}+y\mathrm{FeS}+z\mathrm{Cu}$, then the following equations will enable us to understand the conversion of *blue-metal* into *white-metal* by the action of oxidized compounds of copper and silica:—

$$x\mathrm{Cu^2S}+2\,\mathrm{FeS}+\mathrm{Cu^2}+2\,\mathrm{CuO}+x'\mathrm{SiO^3}=x\mathrm{Cu^2S}+2\,\mathrm{Cu^2S}+2\,\mathrm{FeO},\ x'\mathrm{SiO^3};$$
$$x\mathrm{Cu^2S}+3\,\mathrm{FeS}+3\,\mathrm{Cu^2O},\ x'\mathrm{SiO^3}=x\mathrm{Cu^2S}+3\,\mathrm{Cu^2S}+3\,\mathrm{FeO},\ x'\mathrm{SiO^3}.$$

Hence it will appear that the sulphide of iron may be completely separated from *blue-metal* without the evolution of any sulphurous acid.

5. *Roasting.*—In this operation *white-metal* is melted with free access of air, and without the admixture of any other substance except silica, of which there is always a sensible amount in the state of sand adhering to the pigs of a regulus cast in sand-moulds. From the descriptions which have been previously given, it might be concluded that *roasting* is essentially a process of oxidation, due to the action of atmospheric air at a high temperature; and that this conclusion is correct will be clearly established by the composition of the two products obtained, namely—*blister-copper* and *roaster-slag*.

Blister-copper.—This term indicates the appearance of the surface of the copper, which presents numerous blister-like elevations, caused by corresponding cavities in the substance of the metal underneath.

The following analysis of *blister-copper*, obtained by the roasting of *white-metal*, is by Le Play:—

Copper	98·4
Iron	0·7
Nickel, cobalt, manganese	0·3
Tin and arsenic	0·4
Sulphur	0·2
	100·0

Mr. Napier has published three analyses of *blister-copper*, which, in essential points, agree with that of Le Play. They are as follow:—

	1.	2.	3.
Copper	97·5	98·0	98·5
Iron	0·7	0 5	0·8
Tin and antimony	1·0	0·7	0·0
Sulphur	0·2	0·3	0·1
Oxygen and loss	0·6	0·5	0·6
	100·0	100·0	100·0

Mr. Napier remarks that the oxygen existed in the state of dioxide of copper, dissolved in the metallic copper: a result which *à priori* would hardly have been anticipated; but that sulphur and dioxide of copper may co-exist in metallic copper has already been demonstrated (see p. 264).

Before the copper reaches the state of *blister-copper*, it passes through that of *pimple-copper*, so called on account of the pimple-like excrescences with which its surface is studded. Mr. Napier gives analyses of six varieties of copper produced in the operation of *roasting*, and in a *less advanced* state than *blister-copper*. The extremes of variation per cent. in the copper, iron, and sulphur, are as follow: copper, 89·4—95·6; iron, 0·3—2·4; sulphur, 0·4—2·5. To all such varieties the term *coarse-copper* is applied in contra-distinction to *blister-copper*.

Roaster-slag.—This slag presents a characteristic appearance: it is vesicular, and more or less pumice-like, or scoriaceous; it is without metallic lustre, and its prevailing colour is dark-reddish brown, but here and there it is grey-black.

This slag contains shots of metallic copper, which may be separated by trituration and levigation. Le Play has published the following analysis of *roaster-slag*, which contained but little intermingled metallic copper:—

Silica	47·5
Alumina	3·0
Dioxide of copper	16·9
Protoxide of iron	28·0
Oxides of nickel, cobalt, manganese	0·9
Protoxide of tin	0·3
Lime and magnesia	traces
Metallic copper	2·0
	98·6

Le Play estimates that on an average *roaster-slag* contains 20 per cent. of copper, inclusive of that present in the metallic state. A piece of *roaster-slag* which Mr. Morgan gave me at the Hafod Works, and which he considered to be a characteristic specimen, contained as much

as 43·73 per cent. of copper existing as oxide, and 0·85 as metallic copper: these results were confirmed on repetition. In the following analysis of *roaster-slag* recorded by Mr. Napier, the per centage of copper is 39·95:—

Silica	45
Oxide of copper (Cu^2O?)	25
Oxide of iron (FeO?)	28
Sulphur	2
	100

From the fact that sulphur is stated to be a constituent, it is to be inferred that some metallic sulphide was present; and as the slag is scoriaceous and only *imperfectly melted*, it is not difficult to understand how it should retain intermingled sulphides, notwithstanding the presence of so large an amount of oxide of copper. In the sequel it will be demonstrated that *well-melted* slags essentially composed of silica and protoxide of iron may contain a sensible quantity of sulphide of iron.

From the preceding analytical data, the reactions which occur during the process of *roasting* may be deduced, and a reason assigned for the particular method of conducting that process. The manner in which copper may be completely reduced from disulphide by the joint action of heat and atmospheric air has been fully explained; and it is precisely in this way that *blister-copper* is reduced from *white-metal* in the operation of *roasting*. The chief object, therefore, of the operation is to effect the reduction of the disulphide of copper constituting *white-metal* by the generation of *oxide of copper*. Now, if, in *roasting*, the regulus were *rapidly* melted, the action of the oxygen of the air which enters the furnace would be limited to the surface of the bath of melted regulus; and although reduction would in this case proceed, yet the time required to effect the removal of the sulphur, as sulphurous acid, would be greatly prolonged. But, in the ordinary method of *roasting*, the regulus is, as we have seen, *very slowly* melted, so that every drop as it trickles down is exposed to the action of the free oxygen in the gaseous current of the furnace. A considerable quantity of oxide of copper is thus formed, which decomposes the disulphide in contact with it; and so reduction takes place *pari passu* with the fusion of the regulus. Still, after complete fusion, desulphurization of the product which consists of regulus and metallic copper is far from complete. In the next, or second stage of the operation of *roasting*, the temperature of the furnace being much lowered, the *rising* of the regulus occurs. Owing to the continuous formation and evolution of sulphurous acid during solidification, the undecomposed regulus is thrown up into porous crater-like prominences, whereby the surface exposed to oxidation is greatly increased, and a considerable quantity of oxide of copper is accordingly formed. As the mass is now in a pasty, almost solid state, the superficial oxide of copper does not become mixed with the undecomposed disulphide, and is, therefore, persistent; nor, indeed, if the oxide and disulphide were in contact, would reciprocal decomposition take place, because the

temperature would not be sufficient to produce that effect. In the third stage, the heat of the furnace is increased so as to completely melt the solidified product; and during fusion the oxide of copper formed on the crater-like surface becomes thoroughly intermingled with the remaining regulus, which is thereby more or less completely reduced with the evolution of sulphurous acid. By this mode of proceeding the object of the *roasting* process is attained without the necessity of frequent rabbling, which would be required if the fusion in the first instance were rapidly effected and the product kept in a state of perfect liquidity until the complete expulsion of the sulphur. In the last stage the product is kept well melted with free access of air during the remainder of the operation. Sulphurous acid continues to escape from the surface of the melted mass, producing an appearance of ebullition and a sound like that of frizzling; and, as we learn from the preceding analyses, a sensible amount of sulphur remains in the final metallic product of the *roasting* process. The gas seems to be formed at some depth below the surface of the liquid mass, as every bubble on escaping occasions some degree of spirting. When a pig of blister-copper is broken vertically across, numerous long, narrow, bright tube-like cavities may be seen occasionally on the fractured surface extending from the bottom to the top. A beautiful specimen of this kind is in the collection at the Museum of Practical Geology, presented by Mr. Hussey Vivian. Oxide of copper is formed on the surface, which, by the action of currents in the liquid, may be submerged, and by coming in contact with still remaining disulphide may determine the evolution of sulphurous acid, and give rise to the spirting in question; or possibly oxidation on the surface may be carried to a degree sufficient to produce a little *dry copper*, which, on coming in contact with the subjacent metal containing disulphide (mechanically mixed or dissolved?), would produce the same effect.

The silica of the slag is, as has been stated, derived partly from the sand adherent to the pigs of *white-metal*, and partly from the sand-bottom and other materials forming the interior of the furnace. The presence of this acid may be useful in combining with the oxides and forming a light, pasty slag, which admits of being easily skimmed off. Moreover, it would tend in a material degree to promote the oxidation of the iron.

Best-selected process.—The object of this process is to produce copper of the highest degree of purity; by which is meant, as free as possible from foreign metals. *Best-selected copper* commands the highest price in the market, and is in special request for the manufacture of certain alloys, such as the best qualities of brass, and the white alloy known as German silver; it is prepared, as we have seen, by a special process of purification; and it is generally pretended that it is exclusively produced from the purest ores. That some smelters do employ the purest ores in making this variety of copper may be true; but that others do not, seems very probable from the fact, which is notorious in Birmingham, that copper which is occasionally (I might say, frequently) sold as *best-selected*, is extremely bad. Some of the smelters

know perfectly well that what I now state is correct, as they have suffered pecuniary loss from having had no small quantity of *best-selected copper* returned on their hands at different times. That the *selecting process* would in a certain degree effect the separation of certain metals, such as tin, might be anticipated from various experiments previously detailed, and that it actually does so will be established by analytical data. The process, it will be remembered, essentially consists in the partial reduction of the copper contained in a regulus, having the composition of *white-metal*. After the principles which have now been expounded and proved by analysis, the mode in which this partial reduction takes place will be clearly understood without any further explanation. The metallic copper, which is separated in the *selecting process*, will be found to contain a considerable quantity of tin, if stanniferous copper-ores had been employed to produce the *white-metal*. Metallic copper decomposes sulphide of tin, in a greater or less degree; but whether this sulphide is capable of being *completely* decomposed by any proportion of copper, does not appear. Supposing the regulus, then, to contain tin in the state of sulphide—the state in which it would exist—it would be in a greater or less degree reduced by the metallic copper in the course of its precipitation through the regulus. So also, if the regulus contain sulphide of antimony, this metal would be set free by the reduced copper, with which it would alloy and subside (see p. 260). The copper which is thus reduced and alloyed is termed *bottoms*. The *bottoms* obtained in the *selecting process* generally, not to say always, contain a considerable proportion of foreign metals, namely, tin, antimony, and others; from which we may infer either that *best-selected copper* is not made from the *purest* ores, or that what are called the *purest* ores are in reality *impure*.

A specimen of the regulus (called *regule*) produced in the first running down, as described at p. 330, had the following characters:—its upper external surface was pimpled; the colour of a fresh fracture was dark-grey, like that of disulphide of copper; it was porous and highly vesicular; it contained large irregular cavities, having a red-brown coating, of a metallic lustre, confined almost entirely to their floors; angular particles of metallic copper protruded everywhere into the interior of these cavities, and in some there was filamentous copper; on the bottom of the pig, which had been in contact with sand, there was also filamentous copper. Another specimen from the Hafod copper-works, and produced many years previously, had precisely the same assemblage of characters.

Le Play has given the following analysis of a specimen of *bottoms* obtained in the *selecting process*:—

Copper	92·5
Iron, nickel, manganese	1·6
Tin	0·2
Arsenic	0·4
Sulphur	4·8
	99·5

Mr. Napier has given the following analysis of what he considers a fair sample of *copper bottoms* :—

Copper	74·0
Tin	13·8
Antimony	4·5
Lead	0·8
Iron	2·5
Sulphur	3·9
	99·5

6. *Refining.*—The physical and chemical changes which the copper undergoes during this operation have been so fully described in a former part of this work, that nothing remains to be added on this subject.

The *refinery-slag* is very heavy, and black externally; its fractured surface is vesicular and porous, dull and not vitreous, and deep brown-red, with a purplish hue; where free from cavities, the substance of the slag is well melted and compact. This slag contains numerous shots of metallic copper.

Le Play has given the following analysis of *refinery-slag* :—

Silica	47·4
Alumina	2·0
Dioxide of copper	36·2
Protoxide of iron	3·1
Oxides of nickel, manganese, etc.	0·4
Protoxide of tin	0·2
Lime	1·0
Magnesia	0·2
Shots of metallic copper	9·0
	99·5

The proportion of metallic copper was determined by stamping and washing 10 kilogrammes (22 lbs.) of a mixture of different specimens of *refinery-slag*. A specimen of this slag, which I obtained at the Hafod Works, contained 57·9 per cent. of oxide, existing as dioxide, and 2·65 of metallic copper, making a total of 60·55 per cent. of copper.

In refining *best-selected copper*, no lead should be added as in the case of *tough-cake copper*, which is intended for rolling. When *tough-cake*, which is made of the ordinary description of copper, is laded without addition of lead, it is apt to *rise* on the face of the cake; notwithstanding which it will roll extremely well, but not so well as after the addition of a small quantity of lead. The proportion of lead may be varied considerably without causing an appreciable difference in the rolling quality of the copper, but not without affecting in a very appreciable degree the appearance of the cake on fracture. Some persons profess to be able to decide with certainty concerning the quality of copper from the appearance of its fracture; but a decision on such grounds may undoubtedly prove erroneous. I have often been unable on the most careful examination to detect the slightest difference in the appearance of the fractures of ingots of copper, which I knew differed much in regard to working qualities and degree of purity. Ample proof has already been advanced that the *same* copper

may be made to present widely different appearances on fracture, according to the manner in which it is cast. Temperature alone will suffice to modify the characters of the fracture in a very perceptible degree. One of the best smelters at Swansea, a man of great experience and an acute observer, in writing to me remarks, "you would be surprised how at different temperatures in the lading the appearance of the fracture is altered. If laded *very hot*—that is, what a *copper-man* would call very hot, for, what other people would call very hot, he says is as *cold as ice*—the structure of the copper seems quite altered; and it presents on fracture an assemblage of crystals, larger or smaller, and more or less perfect, which do not in the slightest degree make their appearance when laded at a lower temperature, and which do not at all affect its malleability." That variation in the temperature of a metal at the time of lading, and the consequent variation in the rate of cooling, should thus modify the fracture is very intelligible, for reasons which have been given in an early part of this work.

Experiments on the small scale will not, except in particular cases, afford satisfactory results on this subject. In the *small assay* no such differences are observable as are indicated by the fracture of a cake or ingot, when obtained at different temperatures. An *assay* at the *tough-pitch*, when the copper is too cold to lade well, and one taken when the copper is as hot as it is usually laded, will present no perceptible difference on fracture. The actual amount of copper in both cases is so small that the metal sets immediately, and the rate of cooling in both may be regarded as practically the same.

At my request, my friend Mr. John Keates was so obliging as to prepare for my examination ingots of *best-selected* and *tough-cake* copper, laded at different temperatures into moulds exactly similar in all respects. There were three of each kind of copper: the three of *best-selected* will be indicated, respectively, by the letters *b*, *b'*, *b''*, and the three of *tough-cake* by the letters *c*, *c'*, *c''*. The ingots *b*, c, were laded at the highest temperature which could be conveniently attained in the refining-furnace; *b'*, *c'*, were laded after the greater part of the charge was out, and the metal had cooled down; and *b''*, *c''*, were laded after the metal had cooled down still more, and was not far from solidification. The characters of the fractured surfaces of these ingots were examined and recorded immediately after fracture, which was obtained in the usual way after first nicking the ingots across the under surface. The upper surfaces of all the ingots were flat. The colour of the *best-selected* copper was perceptibly paler than that of the *tough-cake*. All the ingots presented on their fractured surfaces numerous shining grains, which, on close inspection, especially under a lens, are clearly seen to be caused by globular cavities. *b* uneven, more or less columnar, studded with minute globular cavities in every part; *b'*, somewhat less columnar than *b*, but in other respects similar: *b''*, much less columnar and more even than in *b*. *c*, columnar structure distinct, but less so than in *b*, studded with numerous globular cavities: *c'*, not perceptibly different from *c*: *c''*, very similar to *c'*, except along a band across the top, about ¼ inch deep, where it was silky,

like that of the *assay*, at tough-pitch, tolerably even, with scarcely a perceptible trace of columnar structure. The existence of these globular cavities merits special attention; they have frequently been mistaken for crystalline faces. I have never seen the fracture of an ingot of copper free from this porous structure, except when cast in a reducing atmosphere, as described at p. 276.

It was formerly, and for aught I know to the contrary may still be, the practice of persons entrusted with the examination of the copper supplied to the Navy, to rely entirely on the appearances which it presents on fracture in forming a judgment respecting its quality. How far such a method of judging should be considered satisfactory, may be inferred from the following fact, of the truth of which I have received unquestionable evidence:—In execution of a large contract, a quantity of copper was sent to one of H.M. dockyards, and rejected as inferior on account of the appearance of its fracture. The same copper was simply remelted by the smelter who supplied it, and laded at a temperature different from that at which it had been cast in the first instance, and then returned; when it was accepted as good. I have it on good authority, that the proportion of lead and the temperature at which the copper is laded are the two conditions to be attended to in order to produce *tough-cake* copper which shall present a fracture of which the dockyard authorities will approve. I do not for a moment mean to assert that in no case will the fracture afford any certain indication of quality, although I affirm, without fear of contradiction, that very different qualities of copper may present precisely similar fractures.

In the casting of copper, ingot-moulds of copper or iron are employed. Some smelters have assured me that, according to their experience, the ingots are invariably full of *pin-holes* when iron moulds are used, while others of great experience maintain that it is quite immaterial of which metal the mould may be made; and this accords with my own observation. I have examined ingots which have been cast in both kinds of moulds, and I have found no difference, either in their outward appearance or internal structure. However, moulds of copper are, I believe, in most frequent use; they may be readily made by casting the copper in suitable moulds of cast-iron.

The colour of the surface of an ingot of copper is modified by the temperature of the water in which it is cooled. In casting copper in small ingots of the usual form, the moulds are arranged in a frame on the edge of a long trough filled with water, so that they may be easily inverted without being detached, and allow the copper to fall into the water. As soon as the ingots of copper have solidified sufficiently, which occurs in the time required for the filling of three or four moulds, they are thrown into the water. At first, while the water is cold, the surface of the copper has an orange colour; but when the water has become warm, it acquires a rosy tint, similar in kind to that of Japan copper, though much less intense.

In the Museum of Practical Geology is a very fine and characteristic series of specimens, which Mr. Hussey Vivian has presented in illustra-

tion of the operations of copper-smelting as conducted some years ago at the Hafod Works; and of these I subjoin a list, with the names and statements of the amounts of copper which were attached to them at the time they were received:—

Descriptions of Regulus.	Copper per Cent.
Raw-metal (coarse-metal)	39·1
Red-metal	48·1
Blue-metal (this is decomposing, the surface being covered here and there with a blue efflorescence)	59·8
Metal between blue and sparkle-metal: it contains much moss copper	69·1
Sparkle-metal	74·3
White-metal	76·6
Pimple-metal	78·8
Close-regulus (best selecting process)	79·6
Open-regulus (,, id.: both this and the preceding contain much metallic copper)	80·6

Descriptions of Copper.	
Pimple-copper	99·1
Blister-copper (both this and the preceding must be unusually pure)	99·3

Descriptions of Slags.	
Quartz-ore slag	0 47
Vitreous do., containing alumina and zinc (is not alumina always present?)	0·2
Ore-slag, very sharp (rich in protoxide of iron)	0·5
Ore-slag, of ordinary quality	0·3
Metal-slag	2·1
Roaster-slag	23·9
Refinery-slag	71·0

On the Elimination of certain Foreign Metals during the Welsh Process of Copper-Smelting.

This is a subject of great interest in a scientific as well as practical point of view; but it has not, I believe, been so thoroughly investigated as it deserves. Such an investigation could only be properly conducted by a skilful analytical chemist, and would be very laborious; and it would be necessary that he should have constant access to copper-works, in order to be able to select with due care every specimen intended for analysis. If one of our great Welsh smelters could be induced to take an interest in the *science* of his *art* for its own sake, and quite irrespective of any consideration of pecuniary gain, many important questions concerning the metallurgy of copper would soon be decided. Some of these questions, perhaps, may have been solved long ago within the precincts of copper-works, and the results regarded of too much commercial value to be divulged. The Science of Metallurgy in this country has hitherto not only not received much encouragement from the men who have amassed great wealth by the practice of metallurgic arts, but has frequently had to encounter their strenuous opposition; and the opposition, I have generally remarked, has been proportionate to their ignorance of the principles of the processes which they were engaged in carrying on, and their dependence

upon the brains of others for the successful management of their works. It is this class of men, moreover, who affect superior knowledge, and delude themselves with the notion of their being the exclusive possessors of mysteries—a class which, it is to be hoped, is doomed to speedy extinction. Within the last twenty years I have witnessed great changes in the views of many of our smelters, especially the iron-masters, concerning the value of the Science of Metallurgy. In several of the great iron-works skilful chemists have been successfully engaged in investigating problems of interest, and, with but few exceptions, the results have been freely disclosed.

The elimination of arsenic.—Arsenic is generally, if not always, present in the mixtures of ores smelted in this country: it may occur in combination with copper in *true grey copper-ore* (Fahlerz), in small proportion as arseniate of copper, in mispickel ($FeS^2 + FeAs$), in arsenical iron (Fe^4As^3 and FeA), and occasionally in other minerals. Although arsenic is separated in a greater or less degree during the smelting process, yet it appears to be rarely, if ever, completely eliminated; for, according to recent experiments by Dr. Alfred Taylor, distinct traces of the metal may be detected in all commercial copper.[1] Dr. Taylor states that he found arsenic "in not fewer than forty samples of copper, as it is employed by chemists in the form of wire of various sizes, of foil of various thicknesses, and of gauze, coarse and fine." He further states that he detected arsenic in two out of five specimens of electrotype copper. The copper in the forty specimens above mentioned was, doubtless, of the description known in commerce as "tough cake," as it is only this description which is employed in rolling and wire-drawing. He does not appear to have examined any specimens of "best selected copper," so that his experiments do not justify the conclusion to which he has come, "that all the copper used in commerce, the arts, and chemistry, refined or unrefined, contains arsenic." It needs scarcely be remarked that all copper used in the arts has undergone the operation of "refining."

I regret that at present I am unable to offer satisfactory information concerning the degree in which arsenic is expelled at each successive stage of the process of smelting, and the precise reactions accompanying its expulsion.

In the analyses of Lé Play, previously inserted, arsenic appears as a constituent in *coarse-metal*, *blue-metal*, *white-metal*, *blister-copper*, and the *bottoms* obtained in the *selecting* process; but the proportion was only determined in *coarse-metal* and *bottoms*.

I have perceived a strong odour of arsenic in the steam produced on damping the *calcined granulated metal* with water after its removal from the furnace.

In cavities in the *spongy regulus* obtained in the *selecting process* arsenious acid is found condensed occasionally in beautiful crystals and in considerable quantity. I have received the following observations on

[1] Facts and Fallacies connected with the Research for Arsenic and Antimony, &c. By Alfred S. Taylor, M.D., F.R.S., p. 28.

this point from Mr. Morgan, of the Hafod Works. "In the cooling of the pigs of *selected metal*, large cavities are produced near the top of the pig, either by the disengagement of gas from the metal itself, or by means of a portion of steam, which is frequently formed from moisture in the sand into which the metal is tapped. It is on the upper surface, or rather depending from the roof, of these cavities, that they occur; and the thickness of the scale or plate of *metal* which forms the upper boundary or cover of the cavity I have scarcely ever, I think, found to exceed $\frac{1}{4}$ of an inch."

When mispickel ($FeS^2 + FeAs$) is heated to incipient redness, sulphide of arsenic is evolved, which, in contact with atmospheric air, is converted into sulphurous and arsenious acids. Basic arseniate of sesquioxide of iron exists in the product obtained by roasting this mineral at a sufficiently high temperature.

When arsenical iron (Fe^4As^3 and FeAs) is heated to incipient redness, metallic arsenic is volatilized; and when roasted with access of air, much arsenious acid is evolved, with the formation of a sensible amount of basic arseniate of sesquioxide of iron.

When arsenious acid and atmospheric air are passed over sesquioxide of iron or protoxide of copper at a red heat, basic arseniates of these oxides are formed.[2]

When arsenious acid is passed over protoxide of copper at a red heat without access of air, dioxide of copper and basic arseniate of protoxide of copper are formed.[3]

When arsenious acid is heated with sulphate of copper, arseniate of protoxide is formed.

When arseniates of copper and iron are strongly heated with silica, the arsenic acid is displaced and resolved into arsenious acid and oxygen, and silicates of the metals are formed. These reactions must occur during the fusion of products, such as *calcined ore*, *calcined granulated coarse-metal*, &c., in which arseniates may have been generated during the process of calcination.

When fluor-spar is present in the ores, fluoride of silicon may be evolved (see p. 44) during calcination as well as in the fusion of the calcined ore. The sulphuric acid liberated during the former process may act upon the fluor-spar, causing the production of hydro-fluoric acid, and, owing to the constant presence of quartz, of fluoride of silicon. These compounds of fluor may, possibly, tend to eliminate arsenic in the state of fluoride, which, on subsequent exposure to moisture, would be converted into hydro-fluoric and arsenious acids. Faraday states that in his examination of the condensing apparatus erected by the late Mr. Vivian at the Hafod Works he found "most decided indications of fluoric acid" in water from the first shower-chamber connected with the ore-calciner flue.[4] In a refinery at Birmingham, where the sweepings of silversmiths' and jewellers' workshops—technically called "sweep"—are melted in reverberatory furnaces with the addition of

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[2] Plattner, Die metallurgischen Röstprozesse, p. 89.

[3] Plattner, op. cit., p. 150.

[4] Proceedings, &c., ante cit., p. 67.

lead-slags rich in fluor, so great has been the amount of fluorine compounds disengaged that the glass of all the windows in the immediate vicinity which have been exposed to the smoke is corroded and rendered more or less opaque.

The elimination of antimony.—When this metal is present in copper-ores, it, probably, almost always exists in the state of *antimonial grey copper-ore*. It may sometimes occur in ores in which its presence might not be anticipated: thus, I know that it has been detected in copper alleged to have been made exclusively from Burra-Burra ores; and, if the allegation be true, the presence of a sensible quantity of antimony in these fine ores is, I should think, quite exceptional. In Le Play's analyses of the products of copper smelting, no mention is made of antimony. Napier found more than 4 per cent. of it in *bottoms* produced in the selecting process. It may, certainly, be frequently detected in commercial varieties of copper, even in those reputed to be of the best quality. During calcination, it is possible that some of it may be volatilized in the state of oxide (SbO^3); but it passes, undoubtedly, in considerable quantity into the *coarse-metal*. That it is removed in great measure in the *selecting process*, is proved by the analysis of Napier above referred to, and may also be inferred from the reactions which occur when metallic copper is heated with sulphide of antimony (see p. 260).

In 1856 a patent was granted to MM. Beudant and Benoit, French engineers, for "separating antimony and arsenic from copper-ores."[5] The ores are smelted in the usual manner, so as to yield a regulus similar to *coarse-metal*, and from this regulus the antimony and arsenic are separated by one or other of the three following methods:—1st. Metallic iron, wrought or cast, is introduced into the melted regulus, whereby, it is stated, nearly all the antimony and arsenic are precipitated in combination with iron and copper, according to the temperature and state of the regulus. But a small quantity of antimony and arsenic generally remains in the regulus, and this is precipitated by adding 1 or 2 per cent., more or less, of lead or galena, and continuing the action of the iron. By this treatment the patentees affirm that the regulus is almost entirely deprived of antimony and arsenic, a small quantity of antimony and a considerable proportion of arsenic being volatilized during the operation. If the regulus contains much sulphur, some roasted ore is added in order to lessen the amount of iron required to effect precipitation. The precipitated metallic mass of antimony and arsenic is melted with a mixture of ore and iron-pyrites, by which means the copper and iron contained in it are extracted, and "the antimony and arsenic are left nearly pure;" the cupreous regulus thus obtained is treated again in a subsequent operation. 2nd. Lime or roasted ore, or a mixture of the two, is added to the melted regulus, and the surface is covered with charcoal or carbonaceous matter, by which process is obtained "a metallic button, or mass of antimony and arsenic, either pure, or mixed with iron and

[5] A.D. 1856. No. 1061.

copper, in quantity varying with the degree of sulphuration of the matt (regulus) and the quantity of lime and roasted ore employed:" the antimony and arsenic remaining in the regulus after this treatment are precipitated by the addition of a little lead or galena, assisted by the action of metallic iron or by that of the charcoal on the surface. As an example of this mode of treatment, the patentees state "that a grey copper or coarse metal, consisting of 68 parts by weight of protosulphuret of iron, 20 parts of sulphuret of copper, and 20 parts of sulphuret of antimony, was melted, with the addition of 16 parts of lime and 6 parts of roasted ore. A button of antimony weighing 13 parts was obtained, and the operation was completed by the addition of 2 parts of galena and stirring the mixture with a piece of iron." 3rd. A sufficient quantity of roasted ore to saturate the excess of sulphur is added to the regulus, and then metallic lead; antimony and arsenic are precipitated, and carry down with them a quantity of lead, varying with the time which is allowed to elapse after the addition of lead, the state of sulphuration of the regulus, and the quantity of lead added. According to the patentees the operation may be so conducted as to cause a complete precipitation of the antimony with only a very small quantity of lead.

In lieu of metallic lead galena may be added to the regulus, together with roasted ore or lime, or both, and the whole is then covered with charcoal or carbonaceous matter. The precipitated button of antimony and arsenic contains lead, copper, and iron.

The regulus, after having been thus deprived of antimony and arsenic, is smelted in the usual manner.

The operations above mentioned are to be effected in a reverberatory furnace, having at the end furthest from the fire a cavity in the bed for the reception of the precipitated metals, so that they may be readily tapped off. When the regulus is well melted a mixture of lime and roasted ore is added, in the proportion of about 80 parts of lime and 30 of roasted ore for each 100 of sulphide of antimony in the mass. These proportions have been found to produce a good result. After the whole mass, with these additions, is completely fused, its surface is covered with carbonaceous matter and the heat continued; the antimony and arsenic collect in the cavity in the bed, from which they are tapped out; about 2 per cent. of galena is then added to the remaining regulus, which is stirred with an iron tool. A fresh portion of antimony, containing some lead, collects in the cavity, and is tapped out; after which the regulus is tapped out. If the last portion of antimony has carried down a little lead with it, the regulus may be regarded as pure; but if the antimony is free from lead, a small portion of lead should be added to the regulus before it is tapped out of the furnace.

The reactions which occur in this process are generally quite intelligible, which is more than can be declared of many patented "improvements" in copper-smelting. The sulphides of antimony and arsenic are reduced by iron with the formation of sulphide of iron. Iron is the reducing agent commonly employed on the large scale in the preparation of antimony from the native sulphide. The patentees do

not affirm that the regulus is totally deprived of antimony and arsenic by the use of iron alone; but they do affirm that by the conjoint use of iron and lead, or galena, a complete precipitation of these metals may be effected. If galena be added, it would be taken up by the regulus, sulphide of lead combining readily with various metallic sulphides: then, by the action of iron, it would be reduced with the evolution of metallic lead, which, on coming in contact with the sulphides of antimony and arsenic, would effect their reduction; and the excess of metallic lead in subsiding would tend to collect and carry down the antimony and arsenic. The principle of this process is similar to that of making best selected copper; but whether it is more economical or more effective copper-smelters must determine. Iron, it may be stated, will not, as some persons suppose, precipitate copper from every description of copper regulus. When the regulus contains a certain proportion of sulphide of iron, metallic iron will not precipitate a trace of copper from it. Thus, thin hoop-iron in large excess may be kept immersed in melted copper-pyrites without causing the separation of any metallic copper. The regulus resulting from this action is reddish-brown, has a bronzy tint, and contains, it is true, minute *angular*, *not globular*, particles of metallic copper disseminated through its substance: this copper is not precipitated by the direct action of the iron, but is separated in the same manner as that occurring in *blue-metal*.

The elimination of tin.—Ores such as "burnt leavings" (see p. 322) may contain a sensible quantity of peroxide of tin (SnO^2). During the first operation of *calcination*, sulphide of tin may be formed by the action of copper-pyrites or any bisulphide of iron present. When peroxide of tin is heated with sulphur or either of these sulphides, it is converted into sulphide of tin with the evolution of sulphurous acid. During the *selecting process*, the tin is in great measure separated from the *regulus*, and passes into the *bottoms*, which sometimes contain sufficient tin to form a white alloy; and this separation is explained by the reaction which takes place when copper is heated with sulphide of tin.

In 1851 Mr. John Cameron, chemist at the Spitty Copper-Works at Loughor, published a description of crystals of oxide of tin which he had observed in copper slags at certain stages of the process. They were insoluble in nitric acid, and when heated with black flux gave a button of tin. Heated in an atmosphere of hydrogen, they were reduced, and water was formed. Mr. Cameron inferred that they were a *quadroxide* (SnO^4), but this inference was, no doubt, erroneous.[6]

I have received from my former student, Mr. Ridsdale, who was for some years engaged at copper-works in South America, but who now holds an appointment at H. M. Mint, very beautiful colourless, transparent, acicular crystals of peroxide of tin, some of which are ¾ inch in length. They were discovered in the chimney of a copper-roasting furnace, which was undergoing repair, and formed part of an incrustation at the base of the chimney flue, close to the bed. When found

[6] Chemical Gazette, 1851, p. 125.

they were nearly black from the presence of protoxide of copper, with which they were coated. The crystals which I received had been previously boiled repeatedly in nitro-hydrochloric acid to free them from associated matter, and afterwards sifted from some amorphous oxide of tin occurring with them.[7] As the furnace from which the crystals were obtained had been in use a long time, and had been employed to roast regulus produced from various descriptions of ore, it was not possible to ascertain from which ore they had been derived. In an experiment by Smith, in which copper-pyrites was heated in admixture with peroxide of tin, crystals similar in appearance to those above described were obtained. The details are as follow: 368 grains of pure copper-pyrites were intimately mixed by trituration with 148 of dressed Cornish tin-ore, yielding 72 per cent. of metallic tin by dry assay; the mixture was put into a covered clay crucible, inclosed within another, the space between the two being filled with the coarse powder of burnt fire-clay, and the whole was exposed to a strong red-heat during ¾ of an hour. A well-melted regulus weighing 412 grains was obtained. Very delicate acicular crystals adhered to the under-surface of the lid, and a considerable amount of similar, but less delicate, crystals were found lining a cavity in the upper part of the regulus. The fractured surface of this regulus was granular and yellowish iron-grey, except near the bottom, which consisted of brilliant, well-defined, interlacing, lamellar crystals, having a superficial bluish-black colour and some degree of iridescence. The inner surface of the crucible surrounding the regulus was coated with a thin layer of black, opaque, vitreous slag. Sulphurous acid had, doubtless, been formed in this experiment at the expense of the oxygen of the oxide of tin and the sulphur of the sulphides; but, as the regulus has not yet been analysed, it is impossible to state with certainty the reaction.

The elimination of nickel and cobalt.—According to Mr. Hussey Vivian, "nickel and cobalt in quantities of considerable value are contained in copper-ores, either the produce of foreign countries or of England;" and in the smelting of such ores these metals pass in part into the

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[7] Professor Miller of Cambridge, at my request, has, with his usual kindness and promptness, examined these crystals, and communicated to me the following results:—"The supposed crystals of SnO^2 are right-angled prisms, without any other faces, not even faces truncating the edges. The ends are imperfect, being either undeveloped or broken. The light reflected from a face of the crystals is most nearly extinguished by a Nicol's prism, held in a proper position, when the angle of incidence is about 64° 34′ or 65°. If the crystals were not doubly refractive, this would indicate an index of refraction between 2·1028 and 2·1445. In the case of a crystal having double refraction, such a number only approximately indicates the refractive energy of the substance. I was unable to find the optical constants of stannic acid in any of the books upon such subjects. I presume it is difficult to find crystals sufficiently transparent for observation. One fragment bounded by cleavage-planes in the University Collection gave, by a very rough observation,

Index of ordinary ray	2·010
Greatest index of extraordinary ray	2·117

These observations confirm the supposition that the furnace crystals are stannic acid. The lustre also favours the supposition."—Jan. 30, 1861.

refined copper, in part into the slags, and in part into "a product called white or hard metal (bottoms?), commonly used in the manufacture of nails or sold at an inferior price." The Fowey Consols copper-ore is stated to contain, in addition to silver, a sensible amount of nickel, to which the alleged inferior quality of the copper produced from this ore has been attributed. In 1851 a patent was granted to Mr. Hussey Vivian for certain methods of separating nickel and cobalt from copper-ores in the process of smelting.[8] These methods are founded on facts previously well known to persons who had any practical acquaintance with the metallurgical treatment of nickel and cobalt ores in this or other countries, namely, the affinity of nickel and cobalt for arsenic, and the affinity of copper for sulphur. Thus, Lampadius, in 1827, published the following statement. "In lead-smelting at Freiberg (bei der Freiberger Blei-und Bleisteinarbeit) *speise* is formed; whilst the sulphur betakes itself to the lead, copper, and iron, the arsenic combines with the nickel, cobalt, and bismuth."[9] It will be seen hereafter that in the smelting of nickel or cobalt ores, arsenic acts a part exactly analogous to sulphur in the smelting of copper-ores. Mr. Vivian claims as his invention "the separation of nickel and cobalt, or either of them, in the form of arsenurets from ores, slags, regulus, and other combinations or alloys of copper . . . by means of the affinity of nickel and cobalt for arsenic and of copper for sulphur."

In the following details I shall adhere as closely as possible to the language of Mr. Vivian. The process is for the sake of convenience divided into two steps: in the *first* step, an impure arsenical compound containing nickel and cobalt is separated from the mass of matter with which these metals were first associated; in the *second* step, the arsenides of nickel and cobalt are obtained in a marketable state.

Ores, slags, and other compounds containing copper and other metals, the whole or chief parts of which are in an oxidized state, are melted with arsenical pyrites containing sufficient arsenic to absorb the whole, or nearly the whole, of the nickel and cobalt, together with a portion of the copper present in the material; and at the same time iron-pyrites or *raw ore furnace metal* is added in sufficient quantity to yield sulphur to combine with the remainder of the copper, and, lastly, coal or carbonaceous matter for the more complete reduction of the oxides. The melted mass, after skimming off the slag in the usual manner, is tapped into a bed, when the arsenical portion sinks to the bottom of the pigs, and is readily separated on cooling from the superincumbent copper regulus. The arsenical compound thus produced contains nearly the whole of the nickel and cobalt present in the material treated; but should the whole of this compound not have been separated from the regulus, the latter must be re-melted once or twice, and tapped off as above described until the arsenical deposit is exhausted. Mr. Vivian found that in treating an oxide of copper, produced by calcining regulus of copper of 70%,

[8] Obtaining nickel and cobalt. Specification A.D. Nov. 4, 1851, No. 13,890.

[9] Grundriss einer allgemeinen Hüttenkunde. Göttingen, 1827. p. 35.

the addition of 8 cwt. of arsenical pyrites, 12 cwt. of raw ore furnace metal containing about 30°/₀ of sulphur, and 2 cwt. of coal to 20 cwt. of the oxide, extracted nearly the whole nickel and cobalt from the oxide and concentrated them in the arsenical product as required. In treating other products of this class, sufficient sulphur should be present to yield a copper regulus of between 50 and 65°/₀, and sufficient arsenic to prevent the bottom from assuming a coppery appearance and to convert it entirely into a compound, which, when broken, will have a sharp, bright, white fracture.

Copper-ores and regulus containing small quantities of nickel and cobalt, and in which the metals are not in an oxidized state, are smelted in the usual manner of smelting copper-ores until they furnish a regulus of *white-metal* of about 70°/₀. This regulus is then roasted so as to produce a metallic bottom. On the completion of the first portion of the roasting process, when the plug-holes are to be closed and prior to melting for tapping, from 3 to 5 cwt. of arsenical pyrites are added. The contents of the furnace are tapped into an ordinary sand-bed, and, when the pigs are cold, under the first three or four will be found a metallic bottom, in which the largest portion of the nickel and cobalt contained in the regulus originally treated will be concentrated. This metallic bottom consists of a low arsenical compound, easily broken, and presenting a greyish fracture approaching that of cast-iron.

Mr. Vivian states that, as arsenic is generally associated with nickel and cobalt in copper-ores, a certain degree of concentration takes place in any metallic bottoms formed by roasting the regulus of such ores, but only to an inconsiderable extent.

Copper-ores or regulus rich in nickel and cobalt, and in which the metals are not in an oxidized state, generally contain a large quantity of arsenic, and are melted in the usual manner of melting copper-ore, except that the metallic products are not granulated, but run into pigs. At the bottom of one or more of the first pigs a product will be found different from the superjacent regulus; it has a higher specific gravity than the regulus, breaks with a light, white fracture, and consists of nickel, cobalt, and other matters; it separates easily from the regulus, and contains the greater portion of the nickel and cobalt originally present in the ore.

Nickel and cobalt are separated from cupreous alloys on the same principle—namely, that of the production of two compounds; one a regulus of copper and other metals, with little or no nickel and cobalt; the other an arsenical compound or *speise*, containing nearly all the nickel and cobalt originally present. These alloys are treated in any of the above described processes by being placed at the top of the charge of materials when they are first put into the furnace; or by melting the granulated metal with materials containing sulphur and arsenic, and proceeding in the manner detailed, but without the admixture of coal.

The arsenical compounds resulting from these processes usually contain from 1 to 12°/₀ of nickel and cobalt, and from 15 to 50°/₀ of copper, together with iron, antimony, and other matters. These

impure arsenical compounds are pulverized or granulated, and then calcined in the ordinary manner of calcining copper-ores. The calcined product is melted with the addition of sulphur and silica, and with arsenic in amply sufficient quantity to combine with the nickel and cobalt. Sulphate of baryta is recommended as the source of sulphur, arsenical pyrites as the source of arsenic, and common sand as the source of silica. A mixture actually used consisted of 12°/₀ of silica, 10°/₀ of arsenical pyrites, 8°/₀ of sulphate of baryta, to 70°/₀ of arsenical product, and 1 part of coal to 4 of sulphate of baryta. The products of this melting were, *first*, regulus containing copper, antimony, zinc, iron, lead, silver, and other such metals as may have been present, and also a certain small portion of nickel and cobalt; *secondly*, nickel and cobalt speise, together with portions of the other metals, which, it is preferred, should thus pass into the speise, rather than the risk should be incurred of any notable portions of nickel and cobalt remaining in the regulus for want of arsenic; *thirdly*, slag consisting chiefly of iron originally present in the material: the slag is skimmed off in the usual manner, and the regulus and speise are tapped off, when, on cooling, they separate according to their respective specific gravities. The regulus is melted slowly and tapped into a bed, when an arsenical product containing nickel and cobalt will again be found under the first few pigs on the first two or three meltings, after which the regulus will be generally free from nickel and cobalt, and may be treated for copper in the usual manner; and in case it should not be quite free, a semi-arsenical bottom may be taken from it, as in the case of ordinary copper regulus before described, which will free it from the last portions of nickel and cobalt, or nearly so. The arsenical product obtained by this second step will be found to be freed from the greatest portion of its impurities, and will contain a largely increased percentage of nickel and cobalt; but in case it should not be sufficiently pure to be marketable, which will commonly be the case, it is to be again pulverized or granulated, calcined and melted, and otherwise treated in the manner described until a *speise* of the required purity is produced.

The elimination of gold and silver.—In smelting auriferous or argentiferous copper-ores, the gold and silver may be more or less completely concentrated in the *bottoms* obtained in the *selecting* process; but in the absence of this process they will be found diffused through the whole mass of the copper produced. In 1856 a patent was granted to Mr. H. Hussey Vivian and others for the "manufacture of copper, and obtaining gold and silver from cupreous ores."[1] The bottoms impregnated with the precious metals are granulated in cold water and then converted by calcination into oxide, which is susceptible of being pounded to dust in a mortar. An ordinary copper-works calciner is capable of bringing 3 tons of copper into this state in 72 hours. This

[1] Date of the specification Dec. 22, A.D. 1856. The persons associated with Mr. Vivian in this patent were Mr. B. Gustav Herrman, manager of his Silver-Works, and Mr. W. Morgan, manager of the Hafod Copper-Works.

method of oxidizing copper by granulation and calcination is not original, as will be shown hereafter. A mixture consisting of 16 cwt. of the pulverized oxide and 26 cwt. of "sulphurous copper-ore" (containing 30 per cent. of sulphur) is melted, when a regulus (containing about 40 per cent. of copper) is formed. The same result may be arrived at by melting the oxide in admixture with raw ore furnace metal and siliceous matter. A small metallic bottom rich in gold is usually produced in this process. It is recommended to add sufficient "sulphurous material" to change nearly the whole of the oxide of copper into regulus. By calcining and smelting in the usual manner, the regulus is advanced to *white-metal* (of about 70 per cent. of copper), which is subjected to the *selecting process*, so as to furnish *light regule* and *metallic bottoms*. From the ordinary furnace charge of 2 tons, 30 cwt. of regule and from 5 to 6 of bottoms have been obtained with a good result. In these bottoms will be found nearly the whole of the gold originally existing in the ore; but if any sensible amount of it remains in the regule, a *second selecting* will remove it and concentrate it in the bottoms. The patentees state that lead, arsenic, and antimony are generally (collectively or separately) present in the auriferous copper bottoms, and that the presence of these metals materially facilitates the concentration of the gold in the bottoms; and they advise that in the absence of any or all of these metals, lead, in the shape of litharge or ore, should be added in the conversion of the oxide into regulus. The metallic bottoms, thus formed, are again and again submitted to the processes of granulation, oxidation, conversion into regulus, and concentration by selecting, until the gold exists in such a proportion to the copper as to render its separation by any of the well-known methods economical. When silver is present in the bottoms, it is extracted from the regulus prepared from them in the manner above described by a special process which will be hereafter described.

In 1846 I made experiments on a considerable scale on copper containing a large quantity of silver and a small quantity of gold. The metal was in ingots, and was converted into sulphide by heating it in large crucibles, with the addition from time to time of sulphur. When the conversion was only partial, I found that the unchanged metal at the bottom was very much richer in silver and gold than the original ingots, but that the regulus with which it was covered retained a considerable proportion of silver and also a sensible amount of gold.

In 1781 Jars, in his well-known work,[2] proposed a process founded on essentially the same principle as that patented by Mr. Vivian, the separation of copper from gold by converting the former into a sulphide. He writes as follows: "It is more than proved that if we had auriferous copper, this process would be still more advantageous than for silver." The process referred to is that of melting auriferous silver in conjunction with iron pyrites in a small blast-furnace, so as to "mineralize" the silver, *i. e.* convert it into sulphide and allow

[2] Voyages Métallurgiques, 3. p. 285.

the gold to subside. "In case we should have much of these auriferous coppers, as may happen at a mine, the separation of gold from the copper after it (the latter) had been mineralized might be very well effected by means of litharge in a reverberatory furnace; for although gold may have a greater affinity for copper than for lead, yet on being disengaged from the copper through the medium of sulphur, it would unite to the lead which in roasting first acquires the metallic state." The regulus or the *plachmall* freed from gold is directed to be roasted and smelted for copper in the usual manner. Jars thus concludes: "How many argentiferous and cupriferous matters containing gold occur every day in commerce which it is not considered worth while to submit to any process of separation, and which might be most advantageously treated by the method which I have just described!"

It is remarkable how much valuable matter lies entombed in metallurgical treatises now regarded as old and worthless. In the course of this work it will be shown that many a modern patentee has claimed inventions as his own which had been known and practised long before he was born.

I have frequently detected traces, and more than traces, of gold in copper, especially, I think—but I am not sure—in that derived from South American ores. Some years ago Dr. Lyon Playfair communicated to me the following incident relating to the presence of gold in copper. At large chemical works, where sulphate of copper was prepared by dissolving copper in sulphuric acid, an insoluble residue was produced in the process which had been put aside from time to time and had not, fortunately, been thrown away. A small sum was offered by certain persons for this residue, which had not previously been regarded as of much value. Suspicion was excited, especially by the quarter from which the offer proceeded, and it was declined. The residue was examined, and found to contain 700*l.* worth of gold!

Alleged superiority of the copper made by the Welsh process as formerly practised.—A practical smelter of great experience assures me that better copper was made by what he terms the old method of *dry roasting*. The pigs of regulus were exposed, during the greater part of the process of *roasting*, to a less degree of heat than sufficed to melt them, and the roastings were repeated often three times, until *blister-copper* was obtained. The tin, antimony, arsenic, &c., are stated to have been more completely removed than is the case in the modern practice of *wet roasting*, in which the *regulus* is melted down rapidly (not always) and kept *boiling* until the sulphur is expelled and *blister-copper* formed. This method is more economical than the old one, but the quality of the copper is deteriorated.

MISCELLANEOUS NOTICES OF VARIOUS IMPROVEMENTS IN COPPER-SMELTING.

Granulation of regulus.—A patent was granted for this process to Thomas Williams in 1778.[3]

Furnaces.—In 1815 William Bevan the younger and Martin Bevan obtained a patent for heating calciners with the waste heat of melting-furnaces.[4]

Melting coarse-metal with non-sulphuretted ores of copper.—A patent was granted to Joseph James for this process in 1828.[5] The proportions should be such as to yield a regulus having as nearly as possible the composition of pure disulphide of copper. A reverberatory furnace, about 11 feet long and 7 or 8 feet broad, is recommended for operating upon about a ton of regulus in admixture with the proper quantity of ore. The advantages ascribed to the process are, that "the separation of iron, sulphur, and other impurities, from copper ores" is facilitated, and that fuel is economised which would otherwise be required for calcination. It is difficult to understand on what principle such a patent could be granted. The process essentially consists in melting regulus with matters containing oxide of copper, but *roaster* and *refinery-slag* are matters of this kind, and they had been used with the same object long before. However, in 1848 it was again introduced into a patent obtained by Alexander and Henry Parkes.[6]

Furnaces.—In 1838 Nicholas Troughton procured a patent for "improvements in obtaining copper from ores," amongst which is the introduction of a blast, either cold, or, by preference, heated to about 500° Fah., into the closed ashpit of reverberatory furnaces.[7] This contrivance was subsequently claimed in a patent granted to Julius Adolph Detmold in 1843,[8] and again in 1849 in a patent granted to Thomas Symes Prideaux, with the title of "improvements in puddling and other furnaces."[9] The Ebbw Vale Iron Company, in Monmouthshire, purchased Detmold's (?) invention, and, after having for some years applied it to puddling-furnaces, have recently been attacked by Prideaux on the ground of infringement. Costly litigation has ensued, which would have been impossible if the officers of the Crown had been compelled to exercise the least discrimination in the concession of patent rights. It is not consistent with common honesty that the Crown, any more than an individual, should sell the *same* article to two or more persons and coolly leave them to fight for the possession of it. Grievous injustice of this kind has been, and is, so frequently perpetrated in the name of law, that it is high time the reckless system of issuing letters-patent should be amended in accordance with recognised principles of justice.[1]

Furnaces.—In 1843 Edward Budd and William Morgan, of the Hafod Works, obtained a patent for "improvements in the treating or reducing

[3] A.D. 1778, May 7. No. 1191.
[4] A.D. 1815, July 12. No. 3938.
[5] A.D. 1828, July 17. No. 5676.
[6] A.D. 1848, Nov. 11. No. 12,325.
[7] A.D. 1838, May 22. No. 8075.
[8] A.D. 1843, Oct. 18. No. 9911.
[9] A.D. 1849, Aug. 30. No. 12,750.
[1] Since the above was in type a verdict has been given, and in my opinion most justly, in favour of the Defendants.

of copper-ores, and in the construction of furnaces for heating such ores, part of which improvements are applicable to other ores."[2] One of the claims is for a "mode of constructing the bottoms of copper-melting and roasting-furnaces—known as ore-furnaces, metal-furnaces, and roasters—in such manner that the under surfaces may be kept cool by air or other fluid." The sand bottom of the furnace was supported by a bed formed of cast-iron plates. Mr. Morgan informs me that bottoms thus constructed were not found successful, and that they have been abandoned long ago.

It would be sheer waste of time even to notice many of the miscalled improvements in copper-smelting for which patents have been granted in this country during the last 20 years. Some of the patentees display such deplorable ignorance of the first principles of chemistry, and such utter want of practical knowledge, as would seem hardly possible with the present facilities of acquiring information.

Napier's process.

This was patented in 1846,[3] and was for some time carried on at the Spitty Works, at Loughor, near Swansea, where I saw it in operation in 1848. I then wrote the following description of the process, with Mr. Napier's assistance. It consists of four operations, corresponding to the four operations of the Cornish method of assaying copper-ores:—

Sulphuretted ores alone are mixed, as well as practicable, according to the relation between the iron and earthy matters and the silica.

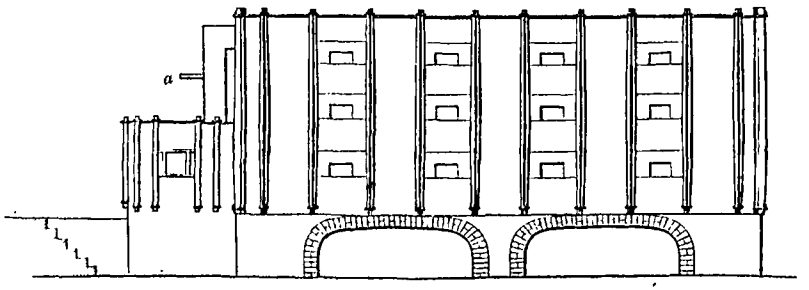

Fig. 98. Side elevation of Great Calciner.

They are then calcined during nine hours, and the calcined ore is melted in the usual way for *coarse-metal*. The slag is skimmed off, and, previously to tapping, for every ton of metal in the furnace are added 120 lbs. of salt-cake (impure sulphate of soda), 40 lbs. of slaked lime, and 60 lbs. of coal. The whole is well mixed by rabbling, after which the furnace door is kept closed for about 15 minutes, when, after again well rabbling, the metal is tapped into sand. When the

[2] A.D. 1813, Dec. 28. No. 9999.
[3] James Napier, "Improvements in Smelting Copper Ores," A.D. 1846, July 20th, No. 11,301.

pigs are set they are put into tanks of water, in which they immediately begin to disintegrate. An alkaline solution is formed, in

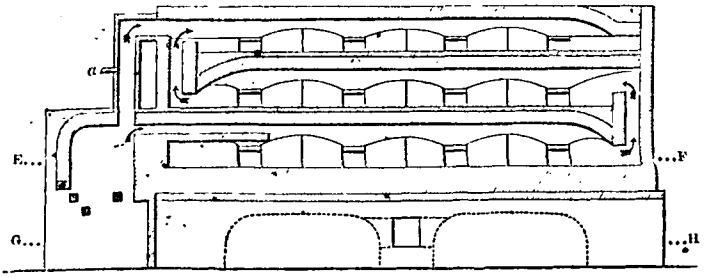

Fig. 99. Vertical section on the line A B, fig. 100.

which, if the ores contained tin and antimony, those metals should be dissolved. The ley, after three or four hours, is drained off and

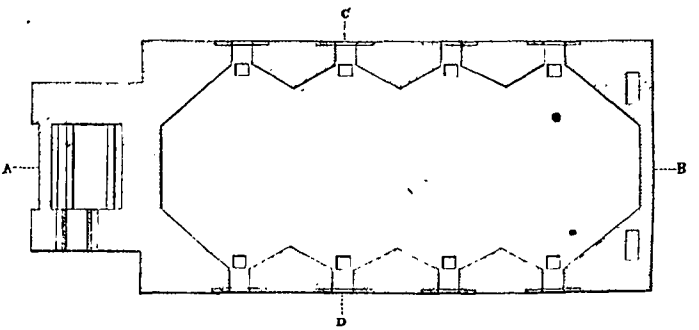

Fig. 100. Horizontal section on the line E F, fig. 99.

thrown away, and the disintegrated powder well washed with water. The washed powder is calcined *sweet*, in large calciners consisting of

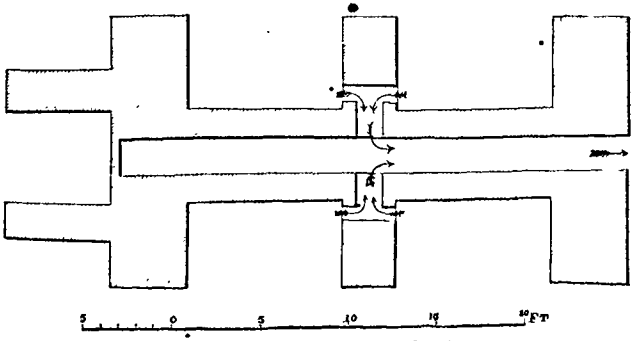

Fig. 101. Horizontal section on the line G H, fig. 99.

three tiers. Engravings of this furnace are annexed. They have been made from drawings which I obtained at the time of my visit to

the works. After the descriptions which have been already given of copper-calcining furnaces, any written explanation would be superfluous. There is only one point to which attention need be called, namely, that the fire-place may, when necessary, be put in connexion with the uppermost bed by drawing out the damper (*a*, figs. 98, 99). Four tons of the powder are calcined during nine hours on each bed in succession, beginning with the uppermost, so that the ore is subjected to a graduated calcination, the temperature of the calciner increasing from the lowest to the uppermost bed. The calcination is continued during 27 or 30 hours for 12 tons of powder. The composition of the washed powder before calcination is nearly as follows, including some adherent silica :—

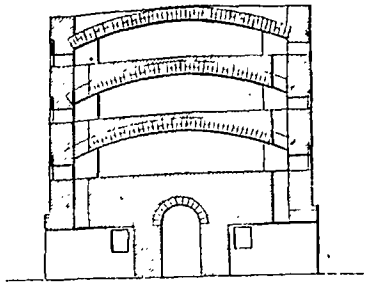

Fig. 102.—Vertical section on the line C D, fig. 100.

Copper	33
Iron	36
Sulphur	27

The calcined powder contains about 45 per cent. of oxide of copper and 52 of the mixed oxides of iron. It is then fused with as much fine anthracite as will reduce all the copper; and some silica is also added in order that it may combine with the oxide of iron and protect the furnace. By this fusion metallic copper is obtained with about 1½ per cent. of metallic iron. If there is a stock of *non*-sulphuretted ores, they are mixed with the calcined washed powder and anthracite. The former act as a flux to the latter, supplying the silica necessary for the oxide of iron produced during the calcination. None of the slags are, in this case, remelted, as on testing, which is never omitted, they are not found to contain a sensible amount of copper. Copper is thus reduced and obtained in a fit state for the refinery. It contains only iron, and no sulphur. It is melted as quickly as possible, care being taken to avoid the presence of carbonaceous matter. The whole is well rabbled from time to time. In about eight or ten hours the iron is found to be oxidized, and, upon the surface of the metal is a slag, which is skimmed off, when, if necessary, poling may commence. Occasionally, however, the iron itself in oxidizing is stated to produce the effect of poling by reducing in a suitable degree the dioxide of copper which may be formed in the copper; for the latter is sometimes found to be at the *tough-pitch* without poling. The sulphate of soda being put into the furnace in admixture with coal, becomes reduced to sulphide of sodium, which is uniformly diffused through the *coarse-metal*, probably in a state of chemical combination. When the pigs are thrown into water the sulphide of sodium slowly dissolves, and the whole mass becomes disintegrated and reduced to impalpable powder. Now,

as the sulphides of tin, antimony, and arsenic are strong sulphur-acids, and as sulphide of sodium is a strong sulphur-base, it was conceived that, in the event of any of these metals being present in the ores, they would be dissolved out during the disintegration and subsequent washing in the form of soluble sulpho-salts. I examined a solution which had been obtained in this manner, and it certainly contained antimony, as might have been anticipated if that metal had been present in the ore. In the course of practice, however, it was, I believe, found that the separation of these metals was far from complete, and, from one cause or other, this new process of copper-smelting was speedily abandoned and the ancient method resumed at the same works. The works were purchased a few years ago by Messrs. Williams and Vivian, who, it is reported, extracted from the furnace-bottoms and other cupriferous materials on the premises a large quantity of copper in excess of the estimated amount; but whether this report be correct or not, I am unable to state. It certainly is not an improbable one. The works have remained closed since they became the property of the smelters above-mentioned.

Method of smelting proposed by MM. Rivot and Phillips.

The method was suggested to these gentlemen—one of whom, M. Rivot, is a professor at the École des Mines, Paris—in 1845, in the course of experiments concerning the proposed application at that time, in England, of the voltaic current as an agent for effecting the extraction of copper from its ores. The following abstract is from a MS. description.

Sulphuretted ores of copper, free from tin, antimony, and arsenic, are to be reduced to powder and roasted sweet. The roasted ore is to be fused in a reverberatory furnace in admixture with lime or sand and slags from a preceding operation, so that the whole of the copper may exist as silicate in the melted mass. Flat bars of iron are then to be introduced into this mass through suitable apertures in one side of the furnace. The copper is displaced from the silicate by the iron, and subsides to the bottom of the furnace, from which it is tapped, an equivalent proportion of silicate of protoxide of iron being formed. Care is to be taken to keep the bars of iron suspended in the melted mass above the surface of the copper, which accumulates underneath, and which, by contact with these bars, would become very ferriferous. It is necessary to throw some small coal upon the melted mass in order to prevent the protoxide of iron in combination with silica from passing to a higher degree of oxidation, of which the effect would be to diminish the liquidity of the mass and to prevent the complete separation of the copper. When copper ores containing tin, antimony, and arsenic are subjected to this treatment, these metals pass more or less completely into the reduced copper. The method was put to the test of experiment in the vicinity of Paris, and the charge of roasted ore operated on at a time amounted to 150 or 170 kilogrammes. It is stated "that the action of bars of iron upon a melted metallic silicate

containing from 2 to 3 per cent. of copper is energetic and rapid, and that 3 hours suffice to reduce the copper in the slag to 0·004 or 0·006 per cent., the copper obtained being free from iron." It was estimated that with ores of 8 per cent. produce the cost of reducing 1000 kil. (about 1 ton) of copper would be 350 francs, and that with ores of 25 per cent. produce the cost would not exceed 112 francs. It was further estimated that, with ores of 8 per cent. produce, the balance in favour of this method, as compared with the Welsh process, would be not less than 175 francs for 1000 kil. of copper! Yet the method has never been adopted, from which it is reasonable to infer that the estimate was erroneous.

Smelting rich Copper-slags in a Blast-furnace.

In 1859 a patent was granted Mr. Hussey Vivian for improvements in copper-smelting, which he describes in the subjoined Provisional Specification.[4] The patent became void by reason of the patentee having neglected to file the complete specification.

Heretofore the ordinary process of smelting sulphurous copper-ores has been to calcine the ore in the first instance to such a degree only as to produce, when smelted, a regulus containing about 33 per cent. of copper, and afterwards again to calcine this regulus, so that when re-smelted it may produce a regulus much richer in copper; from this rich regulus the copper is obtained by other subsequent operations. It is found that if the first calcination is carried so far as to produce a regulus much richer than 33 per cent., the accompanying slag contains a considerable proportion of copper; and as the object of the copper smelter has been to produce slags which may be thrown away without involving much loss of copper, the carrying the first calcining beyond the point above-mentioned has been as far as possible avoided.

Now, according to Mr. Vivian's invention, the ore is calcined in the first instance so far that when smelted it will produce rich regulus, similar to that usually produced after two calcinings and two smeltings, and containing, say, 70 per cent. of copper (unless a somewhat lower regulus for the purpose of making best selected copper be required); and the accompanying slag, which will be rich in copper, is smelted in a blast-furnace, by which operation is obtained from it a further quantity of regulus, and a clean and more uniform slag; and much loss which now occurs from carelessness and mechanical imperfection in slag trying is avoided. The fuel employed in the blast-furnace consists either wholly or in part of the coal and cinders which fall through the bars of the calcining and smelting-furnaces, and which cannot afterwards be conveniently burnt in such furnaces, and are consequently at the present time wasted. The blast-furnace is also employed to reduce the red or coppery slags resulting from processes of copper smelting which are subsequent to the

[4] A.D. 1859. No. 962.

production of regulus, whereby metallic copper is obtained from these slags instead of regulus, as is now the practice. It is stated that the impurities contained in these slags are not by this process re-introduced into fresh lots of copper, as is now the case; and by the reducing action of the blast-furnace many impurities not easily separable in the reverberatory furnace are driven off, and the quality of the copper produced from the slags is improved. Ores of copper which do not contain sulphur are also treated in a similar manner, that is to say, by smelting in a blast-furnace; and thus metallic copper is at once obtained from such ores, in place of, as at present, reducing the copper contained in such ores to the state of regulus, by smelting them with regulus containing an excess of sulphur, which process necessitates the use of a large proportion of sulphurous ores.

In 1859 a blast-furnace was in vigorous operation at the Hafod Works, which at night lighted up the neighbourhood with the greenish flame issuing from its mouth. It is to be regretted that Mr. Vivian has not informed us what those *many* impurities are, which, he alleges, are driven off in the blast-furnace. In a subsequent part of this volume evidence will be adduced to show that certain impurities, well known to affect the quality of copper, are not absent from copper smelted in blast-furnaces. Mr. Vivian may, possibly, possess novel and important information on this subject, which he has not deemed it prudent to disclose. Supposing Mr. Vivian's patent not to have become void, it is difficult to understand how he could have established it on the ground of *novelty of invention*. But the word invention is not unfrequently used in the present day in what may be termed a *non-natural sense*.

COPPER-SMELTING IN BLAST-FURNACES.

In former times all copper was smelted in furnaces of this description, and they are still employed for the purpose in Europe and other parts of the world. In tracing the history of a metallurgic art, nothing is more striking than the gigantic scale of operation at the present day as compared with that of ancient times. But in some countries no progress has been made, and smelting processes are still carried on just as they appear to have been at their commencement. The principles, however, upon which many of these processes are founded and the manipulations practised have remained substantially the same in all ages. In illustration of the truth of these statements the method of copper-smelting as at present conducted by the natives of various parts of India may be adduced. Nothing can be more insignificant than the scale of their operations, and yet, in principle, nothing can be more correct. The Hindoo smelters belong to inferior grades of society, and the nature of their occupation is regarded as incompatible with respectability. I have much pleasure in now presenting an admirable description of Hindoo copper-smelting which I have received from my friend and former pupil, Mr. H. F. Blanford, of the Geological Survey of India, who, being well informed on the subject of metallurgy, under-

stood what he saw, and has, therefore, given an intelligible account of the process; and I regret that I cannot say as much for many of the authors of Indian Reports on similar subjects, so true is it that men without special knowledge are unable to *observe* what they *see*.

Description of a Native Copper Mine and Smelting Works in the Mahanuddi Valley, Sikkim Himalya.

I witnessed the process here described in one of the southern valleys of the Sikkim Himalya, a few miles from the Terai. The workmen were Nepaulese, by one of whom the little mine from which the ore was obtained was rented of government.

The rock of this part of Sikkim, to the north of the great fault which runs along the base of the hills, is a highly foliated quartz and hornblende schist, the folia of which dip at an angle of 30° or 40° towards the north. The copper vein was small, and, apparently, almost coincident with the foliation, dipping evidently at a very low angle. The ore was copper pyrites with a large admixture of mundic (iron pyrites). I was unable to visit the workings, which appeared to be carried on in the rudest and most irregular manner, owing to the fires being lighted at the time of my visit for the purpose of loosening the vein-stone, a mode of "winning" at one time extensively practised in Europe, and still to be seen in some important mines. The vein-stone loosened by the fire was afterwards detached and broken up by means of the hammer and gad, sketches of which I here append (Fig. 103). A small pick of the annexed form (Fig. 104) was also used.

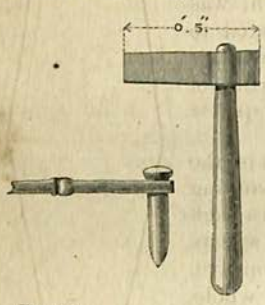

Fig. 103.

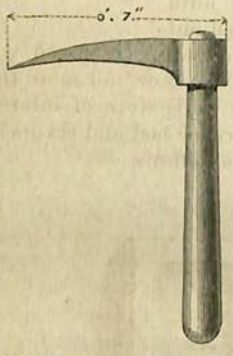

Fig. 104.

The ore as brought from the mine, and which appeared to be very poor, was separated as much as possible with the hammer from the adhering rock, and was then pounded with a heavy stone mallet, another stone, with a slightly hollowed surface, serving as a "knockstone," on the centre of which, after each blow, the ore was swept together by a woman. The ore thus pounded was next washed by women in small tyes, which, in their general form, much resembled those employed by the tin-streamers of Cornwall, but were smaller and of more simple construction. This tye consisted of six planks about one foot in width fixed on edge in the ground, so as to form a partitioned trough of the form here shown (Fig. 105). The cavity above the head-board was nearly filled with clay, over which a stream of water, easily regulated in amount by a little clay placed in the feed-

ing-channel, was allowed to flow, and enter the lower trough through a notch (*a*) in the head-board.

The woman who sat, or rather squatted, by the tye, with one hand divided and directed the stream while with the other she held to the aperture (*a*) a handful of the pounded ore, which was thus washed down into the tye. When a considerable quantity of ore had thus accumulated, it was further washed by being raked up with the fingers towards the head-board, while a good stream of water was allowed to flow over the mass. This was continued until the ore was considered sufficiently "clean." The mass accumulated in the lower part of the tye was thrown away, and that in the upper part, occupying about one-third of its length, was removed to the furnace without being subjected to any further process. It consisted of a small quantity of copper pyrites mixed with a large proportion of mundic, and also much gangue, principally quartz and hornblende.

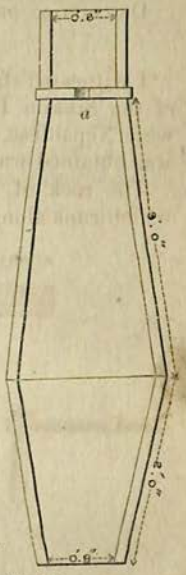

Fig. 105.

The furnace, formed of a sandy clay, was of the form and dimensions shown in the accompanying engravings (Figs. 106 and 107). It was built in a bank about two feet high, and consisted of a shallow square cavity, the bottom of which was slightly concave. The back wall of the furnace—which, as a whole, may be well compared to an arm-chair—was carried up to the height of about eighteen inches, in the form of a truncated pyramid, the top being hollowed out for the purpose of receiving the slags as they were removed with pincers from the furnace. The front wall was very low, not more than about six inches above the bed, while the side walls were of intermediate height, being about one foot above the furnace-bed and six inches above the earthen platform on which rested the bellows.

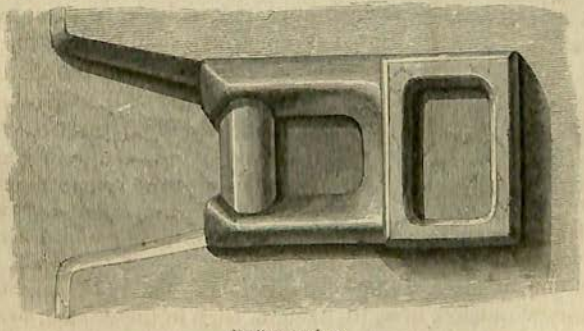
Fig. 106. Bird's eye view.

These bellows were of simple construction, two in number, one being placed on each side of the furnace. They consisted of a seam-

less bag of goat-skin, formed of the skin of the body and fore-limbs of the animal. The bottom, formerly covering the neck of the animal, now embraced in like manner the earthen nozzle of the bellows. The mouth of the bag was gathered in, so as to leave a small opening only, and was grasped by a boy who squatted beside it and worked the bellows, alternately loosening and tightening his grasp as he raised or depressed the bag, thus producing an effectual, though intermittent, blast. The nozzle, moulded by hand, resembled in form the common mouth blowpipe, the end being bent at a right angle, so that, while the stem rested on the side wall of the furnace, the entrance aperture reached to within three or four inches of the furnace-bed, on which the blast impinged at a rather obtuse angle. Charcoal was the only fuel employed in the furnace.

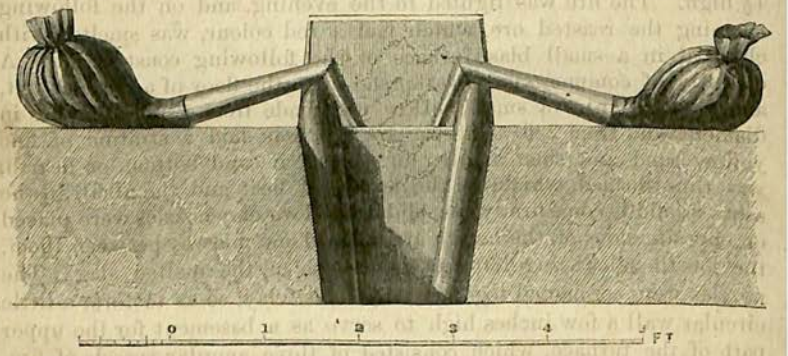

Fig. 107. Front elevation.

The first smelting operation was a simple fusion. The furnace being heated with charcoal, a few handfuls of the washed ore, previously dried and mixed with charcoal, were thrown on, and the bellows worked by boys, as above described. More charcoal was added as required until a perfect fusion of the ore was effected. The fused "metal" (regulus) then formed a small pool at the bottom of the furnace, covered with a layer of fused slag, while the burning charcoal floated on the surface. The fusion being complete, the charcoal was removed, water was sprinkled on the slag to solidify it, and it was then lifted off in successive cakes with a pair of pincers and placed to cool in the shallow basin at the back of the furnace. A fresh charge was then thrown on, and the same series of operations repeated, until a cake of "crude metal" weighing eight or ten pounds had accumulated in the bottom of the furnace. This was removed when cold, pounded, and kneaded with cow-dung into small balls, which were dried in the sun and then roasted in a shallow furnace formed of a ring of slag-cakes placed on edge. The roasted "metal" was afterwards refined in the same furnace in which the fusion of the ore had been effected, and in a precisely similar manner, the result being—1st. refined copper, which collected in the bottom in a cake, weighing four or five pounds;

and 2nd. slag, which was not, so far as I could learn, subjected to any further process, the probability being that the ash yielded by the very large amount of charcoal consumed in the process is sufficient to form a highly basic slag, and thus allow the whole of the copper to be reduced to the metallic state. Three pounds of "crude metal" were said to yield one pound of refined copper.

An excellent account of the native method of copper-smelting at Singhana in India (lat. 28° 5′ N. and long. 75° 53′ E.) was published at Calcutta in 1831.[5] The ore was copper-pyrites with a matrix of quartz. It was reduced to powder, mixed with cow dung, and kneaded by hand into sausage-shaped pieces 5 inches long and 1¼ in diameter. These were sun-dried and roasted in circular heaps 4 feet broad and 1½ high. The fire was lighted in the evening, and on the following morning the roasted ore, which had a red colour, was smelted with charcoal in a small blast-furnace of the following construction. A quantity of common sand was spread upon the floor of a circular hut, and in the centre a small hollow was made from 12 to 15 inches in diameter and from 2 to 3 deep. In this was laid a stratum of fine yellow sand and then another of ashes. A sand bottom, or hearth, was thus formed, which, by the action of heat and the alkali in the ashes, would become firmly consolidated. Two clay nozzles were placed on opposite sides of the hearth and a third one midway between them, the fourth side being left for the escape of the melted slag. The nozzles were connected together with moist clay, so as to form a little circular wall a few inches high to serve as a basement for the upper part of the furnace, which consisted of three annular vessels of fire-clay placed one above another. Each of these vessels was about 15 inches in external diameter, 9 or 10 inches high, and about 3 inches thick. They were used over and over again, but the bottom of the furnace required to be reconstructed daily in the manner above described. Holes were made round the basement, through which a poker might be introduced into the furnace, and there was one such hole obliquely directed through each nozzle near its junction with the furnace, so that a clear passage for the blast might always be maintained. These holes were stopped with clay, which could easily be removed when necessary. The blast was produced by three ordinary goat-skin bellows, of which one was attached to each nozzle. They were worked by men, women, and even children, all Mussulmans. Before the furnace was charged, a quantity of charcoal was burned in the hearth in order to dry it. It is reported that in the day (9 to 10 hours) a single furnace would consume 3 maunds of charcoal (1 mun or maund = 80 lbs. avoirdupois), during which time were added 2½ maunds of the sausage-shaped pieces of ore and cow-dung and 2 or 3 maunds of iron-slag, which was required as a flux, and was brought from a distance. Four persons were employed at each furnace—perhaps a man with his wife and two children—who received for their

[5] Gleanings in Science, No. 36, Dec. 1831. Calcutta, p. 380 et seq.

united services 10 rupees per month. The head man prepared the furnace and occasionally relieved one of the party working the bellows, of which all three were kept constantly in action. On the morning after the first melting, the mass of copper which had collected in the hearth was taken out and sent to the refining furnace. This is described as a small vessel which received the blast of a single bellows. The refined copper was cast into narrow, shallow, clay moulds, each about 1 foot in length. The ingots thus obtained weighed 2 or 3 seers each (1 seer = 2 lbs. avoirdupois). The copper was lilac-coloured and brittle. Copper-smelting must have been carried on in this locality during a very long period, as the slags had accumulated to such an extent as to form a line of small hills several hundred feet in length and from 30 to 60 feet in height. There were four insulated stone bastions built on one of these artificial mounds.

Copper-Smelting in Japan.

There exists a volume containing descriptions of copper-smelting in Japan written both in Japanese and Chinese, illustrated with numerous plates, representing the manner of working, ventilating, and draining the mines, the dressing of the ores, and the process of smelting, together with other metallurgic operations employed in extracting silver from copper by means of lead. An account and partial translation of this work have been given in the 'Chinese Repository,'[6] from which I have derived the following information on the subject. I much regret that I have not had the opportunity of seeing the original volume, which appears to be most complete, as it is stated there are not less than a hundred drawings merely of the implements employed, such as iron ladles, rods, forks, skimmers, pincers, sieves, brooms, tubs, crucibles, moulds, mortars, weights, bellows, &c. Various kinds of ore are obtained, which are described as yellow, black, reddish, and grey, brilliant and dull, rich and poor. After leaving the mine the ore is broken in pieces, from which the barren vein-stuff is selected and thrown away. Generally the best ore yields 10, and the poorest 5, per cent. of copper.

In the first operation the ore is roasted in solidly constructed and permanent kilns, in which are holes for the admission of air. They are built under a shed, and are filled with alternate layers of faggots and ore, a bed of faggots being first spread over the bottom, where a vent-hole is made for the free introduction of air. The smoke is so sulphureous as to suffocate one, and the fire cannot be approached. The roasting continues during 10 days. In the Japanese description the time is stated to be 30 days. In the second operation the roasted ore is melted. This is effected in a large furnace erected on one side of a wall, on the other side of which two large bellows are fixed. A trough is described as leading from the furnace, and the whole is contained within a building. In the plate the furnace is represented as sunk in

[6] From May to December, 1840. Canton. v. 19.

the ground. The furnace being charged with coal (charcoal?) and ore, two tall, powerful men pull the bellows, while a third man stands before the furnace to separate and level the mass. When the fire has reached its strength (*sic*), and the liquid metal has risen and filled the furnace, the earthy scoria floats upon the surface, and, little by little, flows off into the trough. As it flows out it is allowed to cool, or else water is sprinkled upon it, and it is taken out and thrown aside. When the ore is all melted, fresh charges of ore and fuel are added until the furnace becomes filled with good metal. All the scoria and fuel are then pushed off, and water is sprinkled upon the top of the furnace, when a solid crust (of regulus) is formed, which is peeled off by means of an iron rod and taken away. A second crust is produced and removed in like manner, and this process is repeated until the whole of the regulus has been taken out, when a mass of copper will be found at the bottom; but if the ore is poor, there may be none. The *coarse-metal* thus obtained is roasted and melted. These operations are, for the most part, conducted like the roasting of the ore and first fusion. When the furnace is full of liquid metal the top is luted with clay, "leaving a small hole in it in which to put the coal and blast the charge. If there is any scum, take it out immediately and wait till the whole mass is thoroughly fused, then open the furnace and entirely remove the ignited coal and earthy slag, after which wait till the heat has abated a little, and then, sprinkling the surface, take it out in the same manner as when taking out the coarse-metal." [This part of the description is not very clear.] All the preceding operations are carried on at the mine.

The copper is next sent to a foundry, where, under the direction of (government?) officers, it is melted, cast, assorted, and has a price affixed to it according to its quality. No copper is allowed to be privately sold. That which is delivered at Nagasaki and Kwashi is from Besh-shi, Akita, and Nambu, while that which is brought to market for ordinary purposes is from other localities. The number of founders is fixed; "they cannot be lightly increased or diminished lest malpractices should arise." In the foundry the copper is melted under a blast, after which the slag and fuel are removed from the surface of the melted metal, which is taken off in successive crusts by sprinkling with water, &c. The product is fine-metal, which forms a mass a little smaller than the bottom of the furnace, about a cubit broad and half a cubit thick. About 250 cattis (100 cattis = 130 lbs. avoird.) can be melted in the furnace at once, and there are three meltings in a day. The refined copper is again melted in an earthen crucible and cast into ingots. This operation is described as follows:—"A tub of hot water is set near at hand and a square wooden pool made, into which the moulds are placed, and over them a thick hempen cloth is spread. When the copper is melted, the scoria taken off, and the fire reduced, hot water is poured into the pool (not very hot) until it is almost level with the moulds; then the smelter, firmly grasping the crucible with a pair of large iron pincers, pours (the metal) into the moulds, which are previously sprinkled with warm water lest they should crack. After-

wards water is sprinkled upon the bars to cool them, and they are taken out with a pair of iron nippers. Each casting produces 10 or more bars; they are 7 or 8 inches long, and weigh about 10 taels (*i. e.* nearly 1 lb. avoird.) each." The following note occurs in the original:—"If cold water is indiscreetly sprinkled (upon the mould), or if the crucible is cracked, in both cases an explosion will take place; and, because the lives of persons are endangered by such an accident, great care should be used to guard against it." All the copper bars which are sent to Nagasaki and Kwashi are made in this manner. It is stated that some copper contains both silver and lead, and that this is softer, and is hammered into sheets or drawn out into wire.

The use of the hempen cloth is explained by Thunberg, who accompanied the Dutch embassy to Yedo in 1771. After importunate entreaties he was permitted to witness the process of casting copper, which he thus describes:[7]—The copper was melted in a small hearth level with the floor by means of hand-bellows, and directly opposite, in the ground which was not floored, was dug a hole of an oblong form and about 12 inches deep. Across this were laid 10 square iron bars, barely the breadth of a finger asunder, and all of them with one of their edges upwards. Over these was expanded a piece of sail-cloth, which was pressed down between the bars, and cold water was afterwards poured in until it stood about two inches above the cloth. A series of long narrow depressions were thus formed in the cloth between the bars, and into these the melted copper was poured from iron ladles, so that it was actually cast in water. I find there is no difficulty in casting small sound ingots of copper under water in the manner described; and the ingots thus obtained have a very clean, bright surface. The form of the well-known Japan copper ingots corresponds to the above description. The transverse section is nearly an equilateral triangle, the edges being rounded and the upper surface somewhat convex. Two which I have measured are from 8 to 9 inches long and about half an inch on the side. One of these was supplied to me by my friend Harry S. Parkes, H.M. Consul in China. The metal was also cast into ingots of various shapes and sizes according to the purposes for which it was intended. The colour of the surface of Japan copper is rich crimson, due, apparently, to a very thin and tenaciously adherent film of dioxide of copper. In 1757 a patent was taken out by Robert Morris for a "new invented method of fashioning and colouring copper in imitation of Japan copper."[8] The copper made from British ore and purified in the usual way is melted and "run into small moulds, which are fixed in a machine which keeps them moving in a horizontal circle under water," of which the temperature is regulated to the proper degree. When the copper is set, it acquires the rich colour of Japan copper. Ingots of the colour of Japan copper have been made in this country and exported to India. According to the late Mr. Vivian they were about 6 inches long, and weighed about 8 ounces each. The rich red colour was produced by dropping the

[7] Op. cit.

[8] A.D. 1757, Feb. 9th, No. 711.

copper from the moulds immediately on its becoming solid into a cistern of cold water.[9]

Copper-Smelting in Sweden.

The process selected for description is that conducted at the copper works at Åtvidaberg, which are the largest in the kingdom. I have pleasure in stating that Mr. P. D. Malmqvist, director of the smelting department at these works, has revised the following description, and has communicated many important details. Mr. Malmqvist has the reputation of being the best copper-smelter in Sweden. I am also indebted to Mr. Andreas Grill and to the chemist of the works for information on the subject. In 1850 the Swedish copper-smelter Bredberg published an account of improvements introduced at these works between 1844 and 1848.[1] In 1859 Julius Ahrend, director of the smelting-works at Oker, published a description, from personal inspection, of the establishment at Åtvidaberg.[2] I have largely availed myself of both these publications.

The copper ores smelted in Sweden consist exclusively of copper pyrites, mixed with a large amount of iron pyrites and siliceous minerals. The principal mines are at Fahlun and Åtvidaberg, in the old provinces of Dalecarlia and Ostrogothia respectively. The mines of Fahlun are very ancient, and of world-wide renown. The Åtvidaberg Works are situate a few milès distant from Linköping. The Swedish ores are very poor, the average yield of those of Fahlun, when dressed, being 4 per cent. of *black copper*, and of those of Åtvidaberg 5 per cent. At the last locality there are several mines, of which the most important is the Bersbo mine. The ores consist of copper pyrites, iron pyrites, magnetic pyrites, zinc-blende—which in that of the Bersbo mine forms, on an average, one-third of the entire mass—magnetic oxide of iron, quartz, felspar, mica, garnet, rarely calc-spar, and, very seldom, traces of galena. In the ore from one of the mines crystals of bright white cobalt occur together with the copper pyrites; and in the same mine fluor-spar is found, and occasionally arsenical pyrites. The proportions in which these constituents occur in the ores vary considerably. The copper and iron pyrites and blende are sometimes so intimately mixed that they cannot be detected by an inexperienced eye. The ores are divided into hard and soft according as the quartz and hard silicates or the sulphuretted constituents preponderate.[3] The smallest pieces of ore are washed in a cylinder of thin iron bars, moving in water, whereby a separation into two kinds is effected, one of the size of gravel, and the other of the size of walnuts, both of which are used to cover the roast-heaps.

Furnaces.—Three kinds of furnaces are employed, namely, the *ore-furnace*, the *black-copper furnace*, and the *refining-hearth*.

Ore-furnace.—Figs. 108, 109, 110 are copied from Bredberg's engrav-

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[9] Proceedings, &c., ante cit. p. 85.

[1] Bergwerksfreund, 1850, v. 13, p. 410 et seq.

[2] Berg.-u.-hüttenm. Zeitung, Feb. 28, 1859, p. 69 et seq.

[3] Ahrend, op. cit.

ings. Fig. 108, horizontal section on the line A B, figs. 109 and 110. Fig. 109, vertical section on the line C D, fig. 108. Fig. 110, vertical section on the line E F, fig. 108.

This furnace consists of a quadrangular shaft, open above, and below terminating in a shallow cavity called the hearth, *b*, *b*, *b*, from the bottom of which, at one corner, proceeds a channel or tap-hole, *c*, fig. 108. The sides and back of the shaft are formed by walls built up from the ground, while the front is enclosed by a wall supported on a bar of iron, *d*, fig. 110, called the *tymp-iron*. From this bar, to a certain extent upwards, the wall is narrow and vertical; it is called the *fore-wall*, and may be taken down and replaced with facility. Higher up the front wall is much thicker, the inner side inclining inwards and the outer side rising vertically to the top. Where the thin wall ends (see fig. 110) there is an iron girder, *f*, to support the front of the furnace above. At the back, and some distance above the tymp-iron, is an open arched space (*a*, fig. 110), in which four twyers are fixed (*a*, *a*, *a*, *a*, fig. 109). That part of the hearth which extends beyond and to the left of the tymp-iron (*d*, fig. 110) is called the fore-hearth, which is open above. In front of the furnace, above the fore-hearth, is fixed a hood to take off the sulphureous gases which may escape, and which would otherwise greatly incommode the

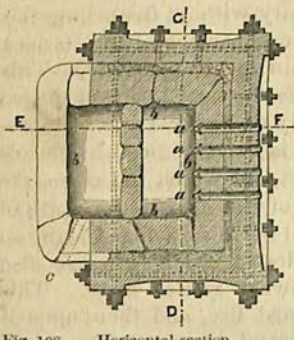

Fig. 108. Horizontal section.

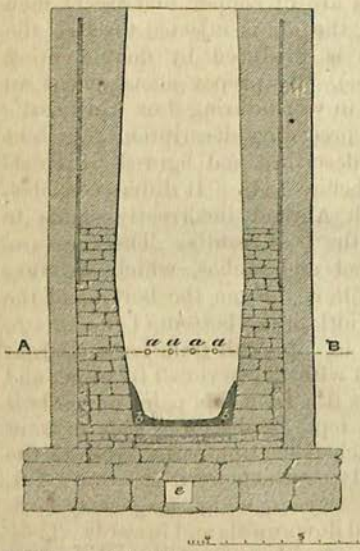

Fig. 109. Vertical section on the line C D, fig. 108.

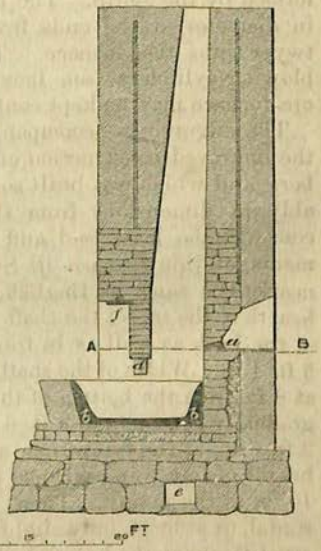

Fig. 110. Vertical section on the line E F, fig. 108.

furnace-men. The interior of the furnace is built of mica-schist, in which the mica is sometimes replaced by talc. The foundation is solidly constructed, and kept dry by means of a drain, *e* (figs. 109 and 110). For a considerable distance downwards from the top the walls are built double, a narrow space being left between the outer and inner walls, which is filled with sand. By this construction the inner walls can be removed when repairs become necessary without disturbing the outer walls, and, space being allowed for the expansion of the furnace by heat, cracks on the exterior are, to a certain degree, prevented. This space is indicated in figs. 109 and 110 by the vertical strips of dotted shading. The dotted shading in the vicinity of the hearth also represents sand. The lower part of the furnace is firmly braced by means of tie-rods and cast-iron plates (see fig. 108), of which the edges are left white in the woodcuts. On the bottom of the hearth a mixture of equal parts of sand and clay is stamped well down in a moist state, so as to form a layer 4 inches thick. The sides of the hearth are also coated with the same mixture in a somewhat wetter state. This lining is carefully dried by a gentle charcoal fire, and then upon it is applied, in the manner described, a second lining, composed of equal measures of clay, sand, and charcoal-dust. The clay mixture is also rammed into the tap-hole, and the pointed end of a stick 2 or 3 inches thick is driven in until the point is within 3 or 4 inches of the inside of the hearth; the stick is afterwards loosened.

The twyers lie nearly horizontal. They are made by bending iron plate, 8 or 9 inches broad and $\frac{1}{8}$ of an inch thick, and fashioning the ends into nozzles; and, as they are at first several feet in length, when the nozzles are burnt away fresh ones can easily be formed by the smith. The blast-pipes are of copper, and are $1\frac{1}{2}$ inch in diameter at the ends from which the air is injected through the twyer into the furnace. The blast is produced by double-acting blowing-cylinders (see IRON SMELTING). By proper management an ore-furnace may be kept continuously in work during 3 or 4 months.

The engravings accompanying the preceding description represent the improved construction of furnace described and figured by Bredberg, and which was built some time before 1848. It differs considerably in dimensions from that which Ahrend incorrectly states to consume the least fuel and to give the best results. The measurements of this furnace in Swedish feet and inches, which are very nearly the same as English, are as follow. From the bottom of the hearth to the top of the shaft 18 ft. Width of the bottom of the hearth, at the back as well as in front, 3 ft. 8 in. Length from back to front 5 ft. 4 in. Width of the shaft on a level with the twyers 3 ft. 10 in., and at 8 ft. from the bottom of the hearth 4 ft.; from this point upwards it gradually contracts to 3 ft. 6 in. at the top. Width from back to front 2 ft. 8 in. at the tymp-iron, above which it continues the same to the height of 5 ft. 6 in., whence it gradually contracts until it is only 1 ft. 10 in. at the mouth. There are three twyers, which are nearly horizontal, or at most, only slightly inclined downwards and inwards. They are 4 ft. above the hearth bottom; 1 ft. 6 in. above the lower edge of the

tymp-iron ; and 1 ft. 9 in. above the top of the fore-hearth. Measured from the centre of the nozzles they are 12 in. apart. The opening of the nozzles rather exceeds 1¾ in. in diameter, and that of the blast-pipes is 1¾ in. There are three ore-furnaces of the kind described above by Ahrend, and four on Bredberg's plan, except that they are furnished with a partition wall in the shaft from the back to the front. This wall, which is 1 ft. thick, commences 10 ft. above the bottom and extends to the top: it causes a more even descent of the charges, and was adopted when coke was first used as the fuel. The present dimensions of an ore-furnace are as follow:—

	ft.	in.
From the bottom of the hearth to the top of the shaft	24	0
do. do. to the partition wall	10	0
do. do. to the twyers	4	0
do. do. to the lower edge of the tymp-iron	2	6
do. do. to the surface of the fore-hearth	2	3
Width of the furnace at the bottom of the hearth	3	8
do. on a line with the twyers	4	0
do. 8 feet from the bottom of the hearth	6	0
do. at the top (inclusive of the partition wall)	6	0
From the back to the front, at the bottom of the hearth	5	6
do. at the surface of the fore-hearth	6	0
do. on a level with the tymp-iron	2	6
do. 8 feet from the bottom	2	6
do. at the top	1	9

Mr. Malmqvist informs me that generally in Bredberg's furnaces there is a larger daily yield and less consumption of fuel than in those described by Ahrend. This year (1861) an ore-furnace of a new construction has been built for the use of hot blast; and one of the larger furnaces has also been adapted to the use of hot blast. It is expected that by this means fuel will be economized. The blast is heated by the waste gases of the furnaces. The poorer ores of this year have rendered it necessary to try every means of lessening the consumption of fuel.

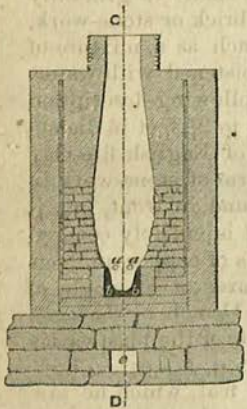

Fig. 111.

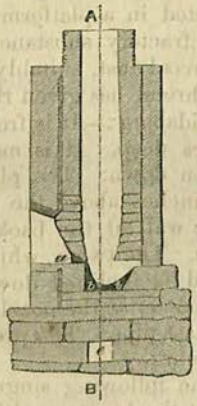

Fig. 112.

Black-copper Furnace. (Copied from Bredberg's engravings.)

Black-copper furnace.—Fig. 111, section on the line AB, fig. 109. Fig. 112, section on the line CD, fig. 108. This furnace is much smaller than the ore-furnace. In the annexed engravings both furnaces are drawn to the same scale as the ore-furnace. The description which has been given of the ore-furnace applies in great measure to this, so that only a few additional words of explanation are required. Hereafter the reader will find more ample details and more elaborate illustrations of blast-furnaces.

The twyers are 10 inches apart, and are inclined towards the interior of the furnace at an angle of $3\frac{1}{2}$ degrees with the horizon. The opening of the blast-pipe is $1\frac{1}{2}$ inch in diameter. The blast is turned full on during the working of the furnace at a pressure equal to a column of mercury of $\frac{7}{8}$ inch (English). From the tap-hole proceeds a channel 36 feet long made of iron plates and divided by partitions into 10 compartments, of which that furthest from the tap-hole is about two inches deeper than that nearest it.

In 1859 one of the black-copper furnaces was enlarged and furnished with a partition-wall and 3 twyers. The dimensions are as follow:—

	ft.	in.		ft.	in.
From the bottom of the hearth to the top of the shaft				17	3
do. do. to the partition wall				6	6
do. do. to the twyers				2	0
Dimensions at the bottom of the hearth	2	4	×	2	0
do. on a level with the twyers	2	10	×	2	6
do. 6 feet above the bottom	4	6	×	2	6
do. at the top	2	6	×	1	6
Thickness of the partition wall				0	6

Since this alteration the consumption of fuel has been diminished 19%, and the daily yield increased 23%. In order in some degree to prevent the reduction of oxide of iron to the metallic state, the gases are partially taken out of the furnace 8 ft. from the top of the hearth and are applied to the heating of steam boilers.

Refining-hearth.—The annexed engraving has been executed from a drawing, supplied by Mr. Grill, of a hearth at Avesta in Sweden, where the ores of the Fahlun copper-mines are smelted. Fig. 113, vertical section on the line G H, fig. 114, which shows the hearth in plan. The figures on the right of the plan are vertical sections of the hearth on the lines A B, C D, and E F, of fig. 114 respectively.

The refining-hearth consists essentially of a shallow, generally semicircular cavity, constructed in a platform of brick or stone-work, and solidly lined with a refractory substance, such as a mixture of finely-pounded clay and charcoal dust, suitably moistened with water, or of fire-clay and sand. Ahrend has given the following description of the refining-hearth at Atvidaberg:—It is from 2 to $2\frac{1}{2}$ feet in diameter, and from 15 to 18 inches deep. It is made of English fire-clay mixed with sand, well beaten down. The platform of stone-work in which it is contained is 16 inches above the ground in front, but it rises somewhat towards the wall at the back; it is entirely covered at the top with plates of iron. The twyer, which is of copper, projects 4 inches over the hearth, and is inclined downwards at an angle of 45° with the horizon: its diameter at the nozzle is $1\frac{1}{2}$ inch, or the same as that of the nozzle of the blast-pipe. The pressure of the blast varies from $1\frac{3}{4}$ to $2\frac{3}{8}$ inches of mercury.

Beckmann has recorded the following singular feat, which he saw performed by the workmen at the Avesta smelting-works in September, 1765:—

"One of the workmen, for a little drink-money, took some of the melted copper in his hand, and after showing it to us, threw it against

a wall. He then squeezed the fingers of his horny hand close to each other; put it (the hand) a few minutes under his arm-pit, to make it sweat, as he said; and, taking it again out, drew it over a ladle filled with melted copper, some of which he skimmed off, and moved his hand backwards and forwards very quickly, by way of ostentation. While I was viewing this performance, I remarked a

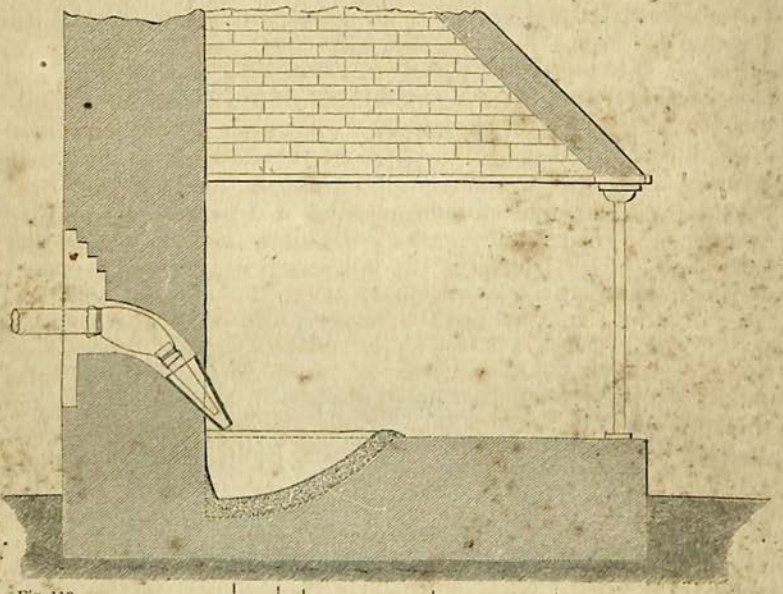

Fig. 113.

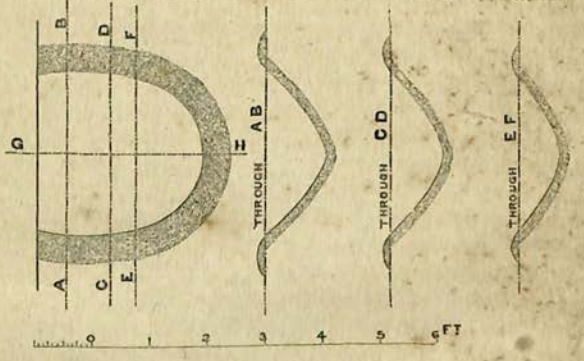

Fig. 114.

smell like that of singed horn or leather, though his hand was not burnt. The workmen at the Swedish smelting-houses showed the same thing to some travellers in the 17th century; for Regnard saw it in 1681, at the copper-works in Lapland."[4]

[4] A History of Inventions and Discoveries. Translation. London, 1814, v. 3, p. 277.

Boutigny, who has of late performed feats of a similar kind, has, as is well known, explained them by the action of water in the spheroidal state.

1. *Roasting, or calcination.*—Ore which is only to be once roasted should be broken in pieces of the size of the fist. Ore which is to be roasted twice may be in larger pieces during the first roasting; but in the second it must be broken in pieces not larger than the fist. Roasting is effected in kilns and heaps, but chiefly in the latter. There are only two kilns, which are constructed as follows:—From each end and the centre of a vertical wall 50 ft. long and 10 ft. high, proceed at right angles three walls 28 feet long, 10 feet high, and 7 feet thick: two rectangular spaces are thus formed, of which each is enclosed on three sides by walls, while the fourth side or front remains open; the upper projecting angles of these walls are rounded off in front. The ground on which the kilns are built is level and horizontal. On the bottom of the kilns wood is piled to the height of 1 foot, and then the largest pieces of ore to the height of 4 feet. On the top of the ore a layer, 4 inches thick, of small charcoal is spread, upon which ore is again piled to the height of 3 or 4 feet, then a second layer of small charcoal, and lastly ore until the kilns are filled. The whole pile is finally covered in front and on the top with a layer 1 or 2 inches thick of the ore dust or schlich. The wood at the bottom of the kilns may now be lighted. Combustion continues from four to six weeks, and at first, owing to the large quantity of zinc-blende present and the free access of air, much smoke is emitted; on the outer surface, as well as in the interior, the ore acquires a white coating of oxide of zinc.

The other kind of roasting, which is the most general, is effected in free, or unwalled pyramidal heaps, from 28 to 30 feet square at the base, and built on level ground. A bed of wood, from 8 to 12 inches thick, is first formed, upon which ore is piled in alternation with layers of small charcoal, just as in charging the kilns, until the heap is raised to the vertical height of from 10 to 12 feet. The sides and top are afterwards covered with a layer of small pieces of ore from 3 to 6 inches thick, and over the whole ore dust is thrown.[5]

Roasting by these methods must necessarily be more or less irregular: in some parts the ore is but little changed, in others it is properly roasted, while in others again it may be sintered or even run together. The roasted ore is broken in pieces not exceeding the fist in size; and the *soft* ore is roasted a second time, which requires three or four weeks. The heaps are prepared in the same manner as in the first operation. The twice roasted ore is broken in pieces of the size of hens' eggs, and is then ready for the next operation: it should retain sufficient sulphur to furnish, when smelted, a regulus yielding from 20 to 30 per cent. of copper. Roasting is a nice operation, and requires considerable attention, which, as at some old works at Fahlun, it does not always receive; but in other localities, where it is properly

[5] Ahrend, op. cit.

conducted, it has been found that the care bestowed upon it is repaid by a better yield of copper.

In former years, according to Bredberg, the roasting of the ore was very carelessly conducted: the large lumps were not properly broken up, and the heat was so irregular, that frequently at the bottom of the pile the ore was found melted into a thick, solid stratum, which required to be blasted with gunpowder, while that at the upper part of the pile had scarcely undergone any change. The consequence was that much of the zinc-blende remained unoxidized, and a refractory substance, termed *skumnas*, rich in sulphide of zinc, was produced in the ore-furnace upon the surface of the melted regulus. It was partly removed along with the slag when the latter was lifted off. It was, in fact, a difficultly fusible regulus, in which zinc in great measure replaced iron; and its specific gravity was less than that of the usual copper regulus. This skumnas, which frequently contained from 10 to 12 per cent. of copper, had during 50 years been thrown away as worthless, so that very large accumulations of it existed in the vicinity of the smelting-works. Within the last 20 years, owing to the improved method of roasting, the skumnas has ceased to be formed, and the copper has been extracted with profit from the old heaps of it which were broken up and assorted, when about one-third was thrown away as valueless, while the remainder, which contained on an average as much as 2·4 per cent. of copper, was retained. Bredberg estimated that about half the copper in the ore had been allowed to escape in the skumnas. The picked skumnas was first well roasted in large heaps, and then smelted in the ore-furnace with the usual constituents of the charge. The formation of skumnas could not be prevented by merely increasing the height of the furnace, though, as has been stated, it was immediately checked by changing the system of roasting, so as to effect more perfect oxidation.[6] Formerly when badly roasted ore was introduced into the furnace, crystalline sulphide of zinc was found sublimed about 4 ft. above the twyers. The formation of skumnas was entirely prevented by roasting the ore rich in zinc blende twice, and the second time with a larger proportion of charcoal.

2. *Fusion of the roasted ore.*—The roasted ore is smelted in admixture with *black-copper slags*, which contain a large amount of protoxide of iron, and are produced in the fourth operation. Although the ore contains much magnetic pyrites and iron-pyrites, the present proportion of silica is so large that sometimes it is necessary to add carbonate of lime as a flux. Formerly, in the time of Bredberg, before coke was used, they could not procure so much fuel as at present, and only the richest ore was smelted; and it was then necessary to add quartz in order to saturate the large quantity of protoxide of iron. The proportions of roasted ore and slags are so adjusted, that a regulus may be formed in which the copper shall not be under 20, nor above 50, per cent.; and a slag, in which the oxygen of the silica shall as nearly as

[6] Bredberg, op. cit.

practicable be double that of the bases. The slag consists essentially of silicate of protoxide of iron; and experience has shown that, when it has the formula $3\,FeO, 2\,SiO^3$, it has the proper degree of liquidity to ensure the most complete separation of the regulus, and that it neither solidifies too rapidly in the fore-hearth, nor corrodes too powerfully the lining of the furnace, nor yet favours the accumulation of ferruginous masses in the hearth to such an extent as to prevent the continuance of the smelting-process during a long period without interruption. Owing to the ascending current of gas containing carbonic oxide (see p. 52), and the presence of incandescent carbon, a portion of the oxide of iron in the roasted ore becomes reduced in its descent through the furnace, and consequently a ferruginous mass, sometimes of considerable size, is formed on the bottom of the hearth.

A mass of this kind is termed "Eisensau" by German smelters. Similar masses occur in the hearths of iron-smelting furnaces, and have received different names in different localities: thus, in Wales they are called "horses," and in Staffordshire "bears." Should the roasting of the ore be carried too far, these masses would accumulate rapidly; and in that case it would be necessary to add some raw ore to the charge of the furnace. Conversely, an increase in the quantity of sulphur in the ore, on account of imperfect roasting, will tend to prevent the formation of "bear." Other refractory lumps occur a little higher up, or follow the slag; and these, which are occasioned by an excess of silica, may be removed by increasing the proportion of protoxide of iron in the charge by the addition of a larger quantity of *black-copper slag*. The ore and slags are mixed and weighed on a steel-yard at each charge; and the number of charges is recorded by means of a peg and a board with rows of holes in it, the peg being advanced one hole at every weighing. The furnace is worked with a "nose" or slag prolongation of the twyer, from 4 to 6 inches long. When the "eye," or point of light seen through the twyer, is "dark," the nose is cleared by poking through the twyer; and if the nose grows too fast, fuel is occasionally added without the usual charge of ore. The appearance of the "eye" affords important indications to the furnace-men. By varying the charge and fuel, the nose may be made longer or shorter at will; and accordingly the blast may be made to enter the furnace at a greater or less distance from the twyer. It is easy to conceive how the working of the furnace should be affected by thus changing the position at which the air impinges on the fuel. By increasing the amount of fuel, the nose may be diminished or even melted off; and, conversely, it follows that an increase in the proportion of slag-producing materials will, *cæteris paribus*, tend to lengthen the nose.

The regulus and slag accumulate in the hearth; and the former, being specifically heavier than the latter, constitutes the lowest stratum. About 60% of the slag is allowed to run out into a sand-bed on the side of the fore-hearth; this slag is considered as *clean*, and is thrown away: it contains from $\frac{1}{4}$ to $\frac{1}{8}$ per cent. of copper. The

remaining slag, as it collects and solidifies in the fore-hearth, is taken off from time to time by means of a two-pronged iron fork, with a long iron handle suspended from a crane: the prongs are about 2½ feet long and 2 feet apart. These crusts of slag must be put aside and remelted in the ore-furnace. They contain from ¾ to 1¼ per cent. of copper. The furnace is not tapped until the hearth has become filled with regulus, which occurs at intervals of from 48 to 72 hours. The amount of regulus which runs out at a time upon a sand-bed varies from 4 to 6 tons. After two days, when the regulus has become cold, it is broken in pieces of about the size of the fist. It is purposely allowed to run over a large surface, so that it may be obtained sufficiently thin to be easily broken in pieces suitable for roasting. The blast being shut off, the tapping is effected by driving with a hammer the point of an iron bar into the tap-hole. The tap-hole is stopped by driving in a piece of wood from 6 to 8 feet long and from 2 to 3 inches thick, and ramming sand round it: after the lapse of an hour the wood may be removed with safety, when the carbonized end will remain in the hole and act as a plug. After the tapping, before the blast has again been turned on, the fore-hearth, breast, and adjacent internal parts of the furnace are cleared from incrusting matter. If the fore-hearth be much injured, it must be repaired with talcose schist, clay, and brasque.

The oxide of zinc in the roasted ore is reduced, and the vapour of zinc, as it rises through the upper part of the furnace, becomes more or less oxidized, and forms an incrustation of furnace-calamine round the interior. Every month this must be detached and removed to the depth of 5 or 6 feet from the mouth. In the course of working, the hearth becomes gradually contracted by the formation of blende-like stony masses, and at length, after the lapse of from 3 to 4 months, the lower part of the shaft becomes so much injured as to make it advisable to blow out the furnace and effect the necessary repairs. The upper part may last several years. The "bear" may be detached without difficulty, and consists for the most part of sulphide of iron and zinc, with very little sulphur, and from 6 to 12 per cent. of copper.

The weight of the regulus varies from 17 to 20 per cent., or even more, of that of the charge. Of late the copper in the regulus has ranged between 20 and 22 per cent.; and in 1859 it did not exceed 18 per cent. In 1860 the ores became still poorer; but there appears reason to believe that this will be only temporary. The slags are stated to contain on an average not more than about ¼ per cent. of copper.

The fuel hitherto employed was charcoal, which of late has been replaced with great advantage by English coke. It has been ascertained by exact trials that in effect 1 cwt. of coke is equal to 2 cwt. of charcoal. This is attributed to the fact that, as coke has a higher specific gravity than charcoal, it yields bulk for bulk more heat than charcoal. To smelt 4 tons of the materials mixed in the proportions previously specified, 1 ton of charcoal is required; but 1 ton

of a mixture of charcoal and coke will smelt 5 tons of the same materials.

3. *Roasting of the regulus from the last operation.*—This is effected in small kilns contained within what is called the Roast-house. In the middle of this house, and extending from one end to the other, is a wall 5 feet high and 3 feet thick, adjoining which on each side are 13 walls, built at right angles, of the same height as the median wall, 11 feet long, and from 2 to 2½ feet thick: there are thus formed 24 compartments, or kilns, 12 on each side, open in front, each of which in the clear is 11 feet long, from 4 to 5 feet broad, and 5 feet high. The bottom is made of a mixture of ore dust and clay, 6 inches thick, so that the height above this bottom is 4 feet 6 inches. In charging a kiln, wood is spread to the height of 8 inches over the whole of the bottom, which should be level: the broken-up regulus is piled on the wood without any charcoal in the first instance. Each kiln contains about 100 Swedish cwt. (between 4 and 5 tons) of coarse regulus. The roasting may now proceed. The process is repeated four, five, or even six times. When the 1st "firing" is finished, the regulus is "turned over," or transferred to an adjoining kiln, in which it receives a 2nd firing, and so in succession until it is roasted as "dead" or "sweet" as practicable, which may not occur until after the 6th firing. In the 1st firing no charcoal is put in; in the 2nd firing ½ measure of charcoal is spread over the wood; in the 3rd firing 5 measures are introduced, partly over the wood and partly forming a layer in the midst of the heap; in the 4th firing 8 measures and in the 5th firing 10 measures are applied in a similar manner; and in the 6th firing 12 measures of charcoal are used, forming 3 layers, including that upon the wood. The entire roasting generally lasts from 7 weeks to 2 months. At each "turning over," the regulus is somewhat broken up, and the kiln charged as in the first instance. As the regulus contains sulphide of zinc, oxide of zinc is formed during roasting, and deposited on the pieces of regulus in the kiln. In the roasting both of copper ore and regulus, it is a remarkable fact that the copper becomes concentrated in the interior of the pieces, forming, as it were, kernels, which, as well in appearance as in the proportion of copper which they contain, frequently resemble purple copper-ore ($3\,Cu^2S+Fe^2S^3$). A special process will hereafter be described, which is founded on this principle of concentration.

4. *Fusion for black-copper.*—The roasted regulus from the last operation is smelted in the *black-copper* furnace in admixture with a roasted regulus, accompanying the formation of *black-copper*, with *refinery* slags, furnace residua containing copper, and *ore-furnace* slags; and, when more silica is necessary, quartz is also added. The proportions of these matters must necessarily vary with the nature of the ore at the time. An actual charge was composed as follows: Roasted regulus, 200 lbs.; roasted *thin* regulus (see p. 406), which is not always added, 40 lbs.; ore-furnace slags, 20 lbs.; cupriferous products, 20 lbs.; quartz, from 10 to 20 lbs. The furnace should be worked with a nose from 4 to 6

inches long. The breast of the furnace is stopped with sand, only a slight opening being left through which the flame blows out. Three products collect in the hearth in the following order of super-position from the bottom, namely, *black-copper*, *thin regulus* containing from 55 to 72 per cent. of copper, and *black-copper slag*. With 55 per cent. of copper this regulus is described as red-blue, and with 72 per cent. as steel-grey: it plays an important part in protecting the subjacent copper from waste by oxidation, and tends to effect the separation of any copper which may exist in an oxidized state in the slag. It is this rich regulus which, after roasting, is added to the charge in the present operation. The yield of *black-copper* may vary from 20 to 30 per cent. of the weight of the charge composed as above stated, but of late it has not reached 20 per cent. *Black-copper* receives its name on account of its superficial black coating of oxide. When the melted matter in the hearth has accumulated to such an extent as to reach the opening from which the flame proceeds, and to rise nearly up to the twyers, the slag is tapped off. This is done by removing the sand with an iron shovel from the breast or fore-part of the furnace, to the depth of 6 or 8 inches below the opening from which the flame issues, when a copious stream of slag flows into cavities in sand previously moulded to receive it. The breast is then closed with sand as before, and the further escape of slag prevented. The slag is subsequently allowed to escape from time to time as may be required. Meanwhile, *black-copper* and *thin-regulus* continue to accumulate in the hearth, until at length they must be removed. Before the final tapping, the slag and regulus are drawn off quite close to the surface of the *black-copper* in the manner just described. After this the tap-hole is opened, when the *black-copper* runs out into moulds of iron, by which means it is obtained in blocks: the tapping is repeated at intervals of two or three days. The *black-copper* is followed by regulus and slag, which run into sand beds. After tapping the blast is stopped in order to enable the smelter to cleanse the hearth. The slag, under which regulus may have collected, is tilted over and broken as soon as it is set, and while still red-hot, so as to separate the regulus as completely as practicable. The slag is rich in oxide of iron, and therefore strongly attacks the lining of the furnace: it contains some copper, and is, as has been stated, remelted in the ore-furnace, in order that this copper may be extracted, and that the necessary amount of oxide of iron may be presented to the silica in the ore. The *bear*, which forms on the hearth-bottom, has a red colour, and consists chiefly of iron, but is rich in copper. The *thin-regulus* is broken up, and mixed with the *ore-furnace regulus* in the third firing, so that it receives only four firings instead of six: but Bredberg states that it is advisable to roast this regulus by itself. The *bear* is heated before the blast of a single twyer in a small hearth open on three sides, when the copper is liquated and the iron oxidized.

5. *Refining.*—The hearth being filled up level with charcoal, thin pigs of *black-copper* are first placed on each side, with their ends pro-

jecting several inches into the cavity, and then three pigs are piled one upon another across the hearth, not too near the twyer. From 13 to 15 cwt. of pigs are refined at a time. Copper residua from previous operations are afterwards added. Ignited charcoal is put in front of the twyer, and cold charcoal thrown on until the *black-copper* is covered with it. The blast is then gradually turned on, so that the metal may slowly melt down. Owing to the great inclination of the blast-pipe, the melted metal is exposed to oxidation, and continues in lively motion. At first the slag has a brownish-black colour, and often a blue tinge from the presence of cobalt; but by degrees it becomes red, in consequence of the formation of a large quantity of dioxide of copper, just as in refining in the reverberatory furnace. The flame acquires a pure and deep green colour; but it is not so variegated at the commencement as in the Lower Harz, and metallic vapour is scarcely ever perceived. The surface of the melted copper must be kept covered with charcoal. The addition of a little broken quartz is occasionally necessary, in order that the slag may have the proper consistency. As no lead is present, a pasty slag mixed with pieces rich in protoxide of iron is formed, which is not sufficiently thin to flow away, as is the case in some Continental refineries, where impure copper containing lead is operated on: the slag is, therefore, removed by skimming twice, and occasionally, when the hearth is large and deep, three times in the course of one refining operation. The skimming is effected as follows: The blast is stopped, all the charcoal is taken out of the hearth, and water is sprinkled over the slag, which being thus rendered solid, may be readily lifted off in the form of a crust. The condition of the melted copper is ascertained by taking out small portions at intervals during the progress of the operation in the same manner as in various copper-works on the Continent. For this purpose a cylindrical piece of iron, with a clean surface and rounded end, is employed: it is plunged through the twyer into the melted copper; quickly withdrawn, and immersed in cold water; the coating of copper which it may thus have received is knocked off and examined. This coating, or trial-piece of copper, is in the form of a hollow cylinder closed at one end, about 3 inches long and ¾ inch in diameter: it is called "Gaarspahn" by the German smelters. If this trial-piece is thick, smooth on the outer surface, and yellowish-red in the interior, the copper is "too young," and must be further exposed to the action of the blast. When it becomes thin, brownish-red, and crinkled on the outer surface, of a pure copper-red in the interior with metallic lustre, and may be bent several times without breaking, the copper may be regarded as refined, or very nearly so. When it becomes so thin as no longer to form a continuous coating, but merely to surround the iron in some places like net-work, and in others to present the appearance of small pointed or bearded excrescences, the blast should be immediately stopped, as the copper is now refined, or "gaar." If the process is continued beyond this point, the outer surface of the trial-piece becomes dull, and acquires a brown-red or reddish brown colour, and the copper cannot be bent without breaking; it is then said

to be "uebergaar," or *dry*. When copper in the hearth is "too young." its surface, freed from slag, appears perfectly tranquil; but in the "dry" state, its surface after removal of the slag presents the appearance of ebullition. At Åtvidaberg, owing to the comparative purity of the copper, the process is sooner concluded than in other localities, where copper containing lead, and it may be other foreign metals, is operated upon; for although the trial-piece may still in a certain degree present the appearances indicative of "too young" copper, namely, a brass-yellow tint and a strong metallic lustre in the interior, the cast copper may, nevertheless, be pure (practically?), and indeed, somewhat over-refined (uebergaar). At Åtvidaberg the black-copper is sufficiently pure to admit of being refined and toughened at one operation. When the pitch is right, the metal is laded into iron ingot-moulds in the same manner as at Swansea. The following analyses of the *black* and *refined* copper (Gaarkupfer) of Åtvidaberg were made at the Mining School at Fahlun:—

	Black-copper.	Gaarkupfer.
Copper	94·39	99·460
Iron	2·04	0·011
Zinc	1·55	..
Cobalt and nickel	0·63	0·110
Tin	0·07	scarcely a trace.
Lead	0·19	do.
Silver	0·11	0·065
Gold not looked for	..	0·0015
Sulphur	0·80	0·017
Arsenic	trace	..
	99·78	99·6645

Oxygen not determined.

The greater part of the cobalt is separated during the process of refining, and becomes concentrated in the refinery slag.

Generally at copper-works on the Continent where the refining-hearth (Gaarheerd) continues to be used, the copper is first refined and afterwards remelted in the same kind of hearth in order that it may be rendered malleable (hammergaargemacht), and suitable for rolling or hammering; but in this hearth the twyer is not inclined, whereby oxidation is prevented. The hearths are generally much smaller than those of Sweden, and the black-copper is often very impure as compared with the Swedish. The process of refining is conducted precisely in the manner described. When much lead is present the slag is liquid, and may be allowed to run off by a channel cut in the side of the hearth. When the trial-piece indicates that the copper is refined, or "gaar," the charcoal is immediately removed, the metal skimmed as clean as practicable, and allowed to cool down to a certain degree, when water is sprinkled over its surface. A superficial solid crust of copper is thus formed, which is lifted off and plunged into cold water. A second crust is produced in the same way and removed; and this operation is repeated until nearly the whole of the copper is withdrawn from the hearth. The first crusts being generally some-

what dirty on the upper surface from adherent matter, they are remelted in the next refining operation. These round crusts or discs of copper are known in commerce as "rosette-copper." They are smooth on the upper surface, with which the water came directly in contact; but underneath, where they were in contact with the liquid metal, they are rough and covered all over with excrescences. Around the circumference is a border directed downwards when the disc is held in the position in which it was formed in the hearth. It is found by experience that when the trial-piece presents the indications characteristic of refined, or "gaar," copper, discs may be obtained having the greatest degree of thinness and presenting a rich red colour, characters which are regarded by purchasers as unerring signs of the purity of the copper. The process of refining is not continued so long as to render the copper very dry, or "uebergaar," but is arrested at a point when the metal may be taken off in the thinnest discs, although it may, as Karsten observes, still retain a sensible amount of foreign metals, which, by a more prolonged exposure to oxidation in the hearth, might, in great measure, be separated. In the dry, or "uebergaar," state thin discs cannot be obtained, and yet this may be solely due to the presence of a large quantity of dioxide of copper, and not in any degree to the presence of foreign metals, or impurities, properly so called; whereas thinner discs, containing only a small proportion of dioxide of copper, may, nevertheless, consist of copper in which a very sensible amount of foreign metals may exist. It is only when the trial-piece indicates that the copper possesses the qualities characteristic of what is termed "gaar" that discs of approved thinness and colour can be obtained. These qualities afford unequivocal signs that the copper has undergone a considerable degree of refining, and, in so far, they may be valuable, but they become fallacious when regarded as sure tests of the degree of purity of the metal. Thin discs cannot be obtained with the purest copper in any state except at a proper degree of heat. Karsten remarks, that "in most European states refined copper (Gaarkupfer) is not cast into bars, but is sent to market in the form of discs; and this practice, once introduced, has led persons to pay attention to the external appearance of the copper rather than its intrinsic excellence. It is required that the discs of copper should be as thin as possible, and possess a fine deep red colour. These qualities are only possessed by absolutely pure copper. The more they are sought for in impure copper the less perfectly will it be freed from foreign matters, and the less will be the tenacity of the metal produced in the process of toughening (hammergaarmachen)."[7]

In the toughening process the discs are slowly melted down under a very gentle blast from a twyer a little less inclined than in the refining process. The form of disc, as compared with that of ingot, is advantageous, as the copper does not press heavily on the charcoal and drop through unmelted, but fuses easily and gradually in every part. When melted it is in the "too young," or overpoled, state (see

[7] Sys. 5. p. 386.

p. 269), but will afterwards pass to the state of tough-pitch by the effect of oxidation, just as, in the Welsh process, in the case of over-poling. Trial-pieces are taken out from time to time in the manner before described, and when the metal has acquired the maximum of toughness it is immediately laded into ingot-moulds. According to Karsten there is a temperature at which it may be cast without "rising" in the mould, but this is so difficult to be attained that it is usual, before lading, to add from a quarter to one-third per cent. of lead, which prevents the rising. The same author also states that the addition of lead renders the copper unsuitable for drawing into fine wire and for plating with gold. When required for these purposes the copper must be allowed to sink in temperature to precisely the right degree, and must then be instantly cast into ingot-moulds.[8] At Åtvidaberg lead is never used in the toughening process, either in the hearth or reverberatory furnace.

Copper rain.—During the time the temperature of the melted copper is allowed to sink to the proper degree, before the commencement of the operation of solidifying the surface with water and taking off the discs, the singular phenomenon called copper rain occurs. Minute spherical particles or shots of copper are projected from the surface of the melted metal on all sides, occasionally, according to Karsten, to the height of 4 feet, and this continues until the surface has become solid. To prevent loss of copper from this cause it is necessary to cover the hearth with sheet-iron in order that the shots may fall back into the melted metal. The same kind of copper rain is produced in the Welsh refining-furnace. In a specimen of it which I have received from Mr. Edmond the particles are pretty uniform in size, and are much less than the smallest pin's head. Karsten gives the following account of the rain and the conditions under which it appears. "The particles vary much in size, and sometimes exceed that of a pin's head, and the higher they are thrown up the larger they are. In other cases a dense red-coloured vapour appears at a short distance above the surface of the melted copper: it consists of innumerable small rotating shots of copper, having a nucleus of metallic copper. The slight coating of dioxide with which the small shots are surrounded is produced by the action of atmospheric oxygen at the moment of their projection. Copper which produces strong copper rain contains but little dioxide; often so little as not to admit of accurate determination. The red dust appears when the copper contains a larger proportion of dioxide. Copper containing from 0·7 to 0·8 per cent. of dioxide still exhibits this appearance in a very perceptible degree. When the proportion of dioxide is still further increased the dust vanishes and the surface of the copper sets quite tranquilly. It seems that 1·25 per cent. of dioxide is necessary to prevent the formation of the rain. All impure copper does not present this phenomenon, especially when it has not taken up any dioxide—the condition in which the strongest rain is evolved from pure copper. All copper which produces rain in

[8] Sys. 5 p. 405.

a remarkable degree is in the malleable state, and might, therefore, be directly cast into ingot-moulds. But copper in this state rises in the mould if it be not poured at exactly the right temperature."[9] This spitting of copper has been discussed in a former part of this work. It occurs when commercial copper is overpoled.

Mr. Grill informs me (1861) that a reverberatory furnace has just been introduced at Åtvidaberg in order to conduct the operation of refining on the Welsh system, and that it is reported to answer extremely well. It is the invention of Dr. C. Th. Boettger, of the Mansfeld Copper-works; it is constructed for the use of charcoal with a view to economize fuel, and has a very high arch.

Consumption of fuel.—In making one ton of copper at Åtvidaberg in 1858 were consumed on an average 240 cubic feet of pine-wood, 7 tons of charcoal, and 3·8 tons of coke. In the table (p. 412) will be found the results of copper-smelting at Åtvidaberg in 1859. It is an exact copy and literal translation of that which was prepared at the works, with the addition of the English weights.

Loss in smelting.—Excepting what may be volatilized, the only loss of copper is in the *ore-furnace* slags, which are thrown away. Mr. Malmqvist estimates the quantity of these slags to be about 50 per cent. of the raw materials, and that, inclusive of the admixture of foul slags, they may be regarded as containing ½ per cent. of copper, in which case the total loss would be about ¼ per cent. of the weight of the raw materials.

Cost of smelting.—This will be subsequently given.

Copper-smelting at Röraas in Norway.—The process is conducted on the same system as in Sweden, and although the ores are richer, yet the yield is not so good as in Sweden. Professor Eggertz, of the Mining School at Fahlun, has published a complete description of the Röraas Works, together with analyses of the products, of which the following is a selection:—[1]

	Ore-furnace regulus.	
	1.	2.
Copper	22·03	20·11
Iron	52·14	52·40
Sulphur	25·15	24·72
Insoluble residue	3·00	3 20
	102·32	100·43

1. Smelted with hot blast. 2. Smelted with cold blast.

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[9] Sys. 5. p. 391.

[1] Jern-Kontorets Annaler for 1849, p. 275. Duchanoy has also published a description of these works, which he visited in 1852. Vid. Ann. des Mines, 5ième s. 5. p. 181.

Results of Copper-smelting at Åtvidaberg in Sweden in 1859.

100 centners Swedish (metal-weight) = 83·7 cwt. English.

Ore roasting.

Number of heaps laid.		Fuel consumed in roasting.	
First time.	Second time.	Charcoal.	Wood in measures of 324 cubic feet Swedish.
		ctrs.	
85	59	31369 cwt.	480·5
		26255·853	"
Ordinary charge.			
Swedish cwt.			

Ore-smelting.

Duration of smelting, day and night, in days of 24 hours.	Materials consumed. Fuel. Coke.	Fuel. Charcoal.	Raw materials. Soft ore.	Hard ore.[1]	Rich ore.	Foul slags.	Slags from black-copper smelting.	Total.	Regulus produced. Average per 24 hours.	Total.	Average percentage of regulus from ores and foul slags.	Fuel consumed to 1 ctr. of regulus. Coke.	Charcoal.	Fuel consumed to smelt 1 ctr. of raw materials. Coke.	Charcoal.
In many furnaces.	ctrs.	ctrs.	ctrs.	ctrs.	ctrs.	ctrs.	ctrs.	ctrs.	ctrs.	ctrs.		ctrs.	ctrs.	ctrs.	ctrs.
1725	79189·60 cwt.	32228·90 cwt.	140273 cwt.	176496 cwt.	44023 cwt.	119351 cwt.	75384 cwt.	565132 cwt.	69·0 cwt.	119092·0 cwt.	24·32	0·665 cwt.	0·270 cwt.	0·140 cwt.	0·056 cwt.
..	66281·695	26975·549	124941·501	147727·152	36851·436	100393·997	63096·408	473015·484	57·753	99630	..	0·556	0·225	0·117	0·046
Ordinary charge.															
Swedish cwt.	0·30 or 0·60		0·60	0·60	0·20	0·40	0·20 to 0·40	2·00 to 2·20							

Regulus roasting.

In heaps. Number at 100 ctrs. each.	Fuel consumed. Charcoal.	Wood in measures of 400 cubic feet Swedish.
	ctrs.	
1204	32256 cwt.	455
..	26998·272	..

Black-copper smelting.

Duration of smelting, day and night, in days of 24 hours.	Consumed. Fuel. Coke.	Fuel. Charcoal.	Raw materials. Roasted regulus.	Residua rich in copper from other processes.	Slag from ore-smelting.	Total.	Black-copper produced. Average per 24 hours.	Total.	Average percentage of black-copper from regulus and residua.	Fuel consumed to 1 ctr. of black copper. Coke.	Charcoal.	Fuel consumed to smelt 1 cwt. of raw materials. Coke.	Charcoal.
780	ctrs. .. cwt. ..	ctrs. 50935·5 cwt. 42633·013	ctrs. 120400 cwt. 100774·8	ctrs. 14613 cwt. 12231·081	ctrs. 14667 cwt. 12276·279	ctrs. 149680 cwt. 125282·16	ctrs. 34·47 cwt. 28·851	ctrs. 26885·20 cwt. 22502·912	19·91 ..	ctrs. .. cwt. ..	ctrs. 1·89 cwt. 1·581	ctrs. .. cwt. ..	ctrs. 0·32 cwt. 0·267
Ordinary charge.													
Swedish centners ..	0·60	2·00	0·20 to 0·40	0·20 to 0·40	0·20 to 0·40	silica. 0·00 to 0·05 to 0·10							

Refining process.

Materials consumed. Charcoal.	Black-copper.	Refined copper produced.	Charcoal consumed to 1 ctr. of refined copper.	Average percentage of refined copper. From black-copper.	From regulus.	From ore.	From ore and slags, forming the charge.
ctrs. 11088 cwt. 9280·656	ctrs. 26885·20 cwt. 22502·912	ctrs. 22981·27 cwt. 19237·833	ctrs. 0·48 cwt. 0·401	85·50	19·09	5·82	4·64
..	..	..	..	..	..	..	..

[1] The soft-ore is roasted twice,—the hard-ore, which besides silica contains much magnetic pyrites, is roasted only once,—and the third sort is not roasted at all, as it consists chiefly of copper-pyrites, quartz, and other siliceous matters, and contains only a trifling quantity of other sulphides. Hard-ores are so called on account of the presence of quartz in large quantity.

	Ore-furnace slag.		Black-copper slag.	
	1.	2.	3.	4.
Silica	28·48	28·18	30·85	23·95
Alumina	9·58	9·46	4·00	4·98
Protoxide of iron	50·99	51·17	66·25	70·74
Lime	1·18	1·41	0·47	0·42
Magnesia	11·55	11·35	,,	,,
Copper	0·38	0·60	0·63	1·06
	102·16	102·17	102·20	101·15

Nos. 1 and 3 smelted with cold blast. Nos. 2 and 4 smelted with hot blast. In Nos. 3 and 4 the magnesia was estimated with the iron. The excess is attributed to the use of water which had not been distilled.

Smelting of Copper-schist in the district of Mansfeld, Prussian Saxony.

This schist is the well-known Kupferschiefer of the Germans, and appears to be the equivalent of the marl-slate of English geologists. It occurs in the Permian series, formerly known as the Lower New Red Sandstone. It is a thin dark-coloured bed of a schistose or slaty structure, lying upon quartzose conglomerate (Rothliegende), and overlaid by limestone. By the miners it is usually divided into four strata, which have received different names in different localities. Thus at Eisleben, in the order of their downward succession, they are designated *Noberge*, *Schieferkopf*, *Kammschale*, and *Letten*. Overlying the uppermost of these strata, the Noberge, is a bed called the Dach, which, though consisting chiefly of limestone, nevertheless forms part of this schistose formation, and is sometimes included, as at Sangerhausen, in the term Kupferschiefer.

The bed of copper-schist proper varies in thickness from 10 to 20 inches, of which only from 3 to 5 inches are worth smelting. It consists chiefly of clay, silica, and limestone, and contains oxide of iron, black bituminous matter, and water. Copper exists in the schist chiefly in the state of vitreous copper (Cu^2S) and purple copper-ore ($3Cu^2S+Fe^2S^3$), but it also occurs as copper-pyrites, grey copper-ore, black copper-ore—a mixture of protoxide of copper with oxide of iron and manganese—red copper-ore, and native copper. The schist is not only cupriferous, but argentiferous, and generally in a sufficient degree to allow the silver to be extracted with profit. The silver is rarely met with in the metallic state. The following minerals have also been found in the schist, either as constant or as occasional constituents:—iron-pyrites, blende, rarely galena, kupfernickel, iron-ochre (a mixture containing sesquioxide of iron), nickel-ochre, smaltine or tin-white cobalt (Glanz-cobalt, consisting essentially of cobalt, arsenic, and sulphur), red earthy cobalt (a mixture containing oxide of cobalt), sulphide of molybdenum, and, very rarely, native antimony, bismuth, and arsenic, and, lastly, according to Kersten, vanadium. The schist of any one particular locality may contain only a portion of

the minerals above mentioned.[2] The metallic minerals are sometimes so finely disseminated as to be imperceptible; or they occur in little veins, in thin laminæ, in nests, or in nodules. Fossil remains of fishes and plants are met with in copper-schist, and, less frequently, those of mollusca.

The sandstone upon which the copper-schist immediately rests is sufficiently cupriferous to the depth of two or three inches to be extracted with advantage. It is called sand-ore (Sanderz), and contains vitreous-copper, purple-copper, copper-pyrites, blue and green carbonate of copper in small rounded nodules, rarely native copper, iron-pyrites, blende, galena, kupfernickel, and native bismuth; but of these minerals the most frequent are vitreous-copper and copper-pyrites. The particles of quartz composing the sand-ore are cemented together either by argillaceous or calcareous matter. The proportion of copper in the sand-ore decreases downwards so rapidly that at Sangerhausen, whilst the uppermost layer of about the thickness of half an inch yields 12 lbs. of copper per centner, that at about 2 or 3 inches below yields only 2 lbs. per centner. So long as the sand-ore contains 4 lbs. of copper per centner it is broken into pieces of from one to half a cubic inch in size and smelted. Poorer sand-ore is dressed preparatory to smelting.[3] The general average of copper in all the sand-ore smelted is about 6 lbs. of copper per centner.[3] A specimen from Sangerhausen in my collection, labelled "Sanderz," consists of a layer of dark grey earthy matter to which is attached one of iron-pyrites. By digestion in nitric acid it was partially dissolved: the washed and ignited insoluble residue amounted to 43·92 per cent.; it was nearly white, very gritty to the touch, presented minute particles of mica, and evidently consisted almost entirely of siliceous sand. Copper and iron in considerable quantity were found in the solution. Another specimen was digested in nitro-hydrochloric acid without having been previously reduced to powder, when rounded particles, apparently of colourless quartz, were observed in the insoluble residue.

According to Heine the Noberge at Sangerhausen consists chiefly of carbonate of lime, with scarcely any silica, and only very little clay; and the copper which it contains exists for the most part as grey copper-ore (Speise), but vitreous copper in grains is also present. A specimen of Noberge from Sangerhausen in my collection is very dark grey in colour, and distinctly stratified. It effervesced on the addition of hydrochloric acid and partially dissolved. The washed residue, after having been heated to redness in a covered crucible, amounted to 55·42 per cent., which was reduced to 53·42 per cent. by subsequent ignition in an open crucible. The solution contained chiefly lime, with a little copper and iron. The ignited residue was pale brown, gritty to the touch, and contained minute scales of mica.

Copper-schist is worth smelting when it does not contain less than 2 lbs. of copper per centner.[4]

The Dach at Sangerhausen, according to Heine, is almost entirely

[2] Vide Die Lehre von den Erzlagerstätten, Bernhard Cotta. Freiberg, 1855, p. 234 et seq.

[3] Heine, Ann. der Phys. u. Chem. Poggendorff, 1835, 34, p. 531. Cotta, op. cit.

[4] Heine, op. cit.

composed of carbonate of lime, and, as a general rule, contains only grains of vitreous-copper; but it is also stated to contain copper-pyrites, purple copper-ore, red copper-ore, malachite, rarely blue carbonate of copper, iron-pyrites, and some galena.[5] A specimen in my collection from Sangerhausen, labelled "Oberberge,"[6] is compact and brownish grey, like an ordinary clay iron-ore. It contains irregularly diffused small patches and minute particles resembling vitreous copper; it effervesced considerably on the addition of hydrochloric acid, and partially dissolved: the washed and ignited insoluble residue amounted to 35·32 per cent. Lime, magnesia (in considerable quantity), iron, and copper were found in the filtrate.

The smelting of this cupriferous schist has been carried on at least during several centuries. Agricola, writing about the middle of the 16th century, minutely described the manner in which, at Eisleben and in the neighbourhood, it was burned in heaps preparatory to smelting.[7] The existing smelting-works are situate in the vicinity of the towns of Mansfeld, Eisleben, and Sangerhausen. Owing to the recent introduction of new methods of extracting silver, this metal, as well as copper, is now obtained from all the copper-schist raised in the district; whereas formerly it could not be extracted with profit from the schist near Sangerhausen, which contains less than that of the other localities mentioned, and which, consequently, was smelted for copper alone. The smelting of sulphuretted ores of copper in the blast-furnace has always been conducted in essentially the same manner as at Åtvidaberg, so that it will not be necessary to enter into much further descriptive detail upon the subject.

The process formerly practised at Sangerhausen and some other localities consisted of the following operations:[8]—1. Roasting of the copper-schist. The ores which did not contain much bituminous matter were not roasted. Some of the schists were sufficiently bituminous to continue to burn of themselves after having been once ignited. 2. Fusion of the roasted ore with slags and fluor-spar. The products were a regulus, containing from about 30 to 35 per cent. of copper and poor slag. 3. Roasting of the regulus of No. 2 in three successive fires. 4. Fusion of the roasted regulus with slags. The products were a concentrated regulus (Spurstein), containing from about 50 to 60 per cent. of copper, and a slag (Spurschlacke) containing from about 1¼ to 2½ per cent. of copper, which was resmelted. 5. The regulus of No. 4 was roasted in seven successive fires. 6. Fusion of the roasted concentrated regulus of No. 5 with slags. The products were black copper and a rich thin regulus (Dünnstein) containing about 63 per cent. of copper, which was roasted along with the regulus of No. 5 in the last three fires. 7. Refining of the black copper. The products were rosette copper, and slags or skimmings rich in

[5] Cotta, op. cit.

[6] A distinct bed forming the upper part of the Dach at Sangerhausen, but not appearing in other districts.

[7] Georgii Agricolæ De Re Metallicâ. Basileæ, 1561, p. 218. The date of the first edition is 1555.

[8] Vide Notice sur les Mines de Schiste Cuivreux et sur les Usines du Pays de Mansfeld. Par M. Manès. Ann. d. Mines, 1824, 1. ser. 9, p. 1 et seq.

dioxide of copper. 8. Remelting of the rosette copper and toughening (Hammergaarmachen). The products were malleable or tough copper, and slags or skimmings rich in dioxide of copper.

At Mansfeld and Eisleben the regulus produced in operation No. 2 of the Sangerhausen process was roasted six times successively; and the roasted product (Gaarröst) was smelted with slags, when black-copper, accompanied as usual with thin regulus, was obtained. At some establishments the regulus was washed with water after each roasting, except the first and last, so that any sulphate of copper present in it might be dissolved out and crystallized. The silver became concentrated in the black-copper, from which it was separated by the ancient process of liquation with lead hereafter to be described.[9] In 1831 this process was discontinued, and the silver was extracted from a concentrated regulus by means of mercury. More than twenty years afterwards the use of mercury was abandoned, and the regulus was desilverized by the wet method of Augustin, which, after three years, was replaced by that of Ziervogel. At the present time (1861) the process of desilverization is only conducted at the Gottesbelohnunghütte, near Hettstädt; so that at the various smelting-works in the vicinity the smelting of copper-schist is not carried further than the production of a regulus, which is sent to the establishment above-mentioned.

In illustration of the treatment to which the copper-schist is now subjected, I insert the following description of the practice at the Kreuzhütte, near Hettstädt, in 1860: 1. The schist contains about 200 lbs. (Prussian) of copper per Fuder, *i. e.* about 3 per cent.: it is roasted in pyramidal heaps containing from 6000 to 21000 ctrs. each; the time required for this process varies from six weeks to three months. 2. The roasted schist is smelted in blast-furnaces about 20 feet high in admixture with fluor-spar, slags accompanying the formation of concentrated regulus and black-copper, and desilverized residua.

The furnace is cylindrical from the mouth down to the top of the hearth, of which the section is square. The dimensions (Prussian measure) are as follow: diameter *at the top*, 3 ft.; *below the top*, at 10 ft. 6 in., 5 ft.; at 11 ft. 6 in., 5 ft. 8 in.; at 14 ft., 3 ft. 9 in.; *at the bottom*, 2 ft. 6 in.—total height, 19 ft. There are two twyers, opposite each other, one on each side, at 2 ft. 2 in. from the bottom; the diameter of the nozzles is from 1½ to 2 in. The bottom of the hearth inclines forwards; and in front are two pits, of which the vertical section is that of an inverted cone; they are about 18 in. in diameter at the top, and 2 ft. deep. The melted matter is not left to accumulate in the hearth of the furnace, but *flows out continuously*, first into one of these conical pits and then into the other, the two pits being alternately filled and emptied. There are, consequently, two apertures at the bottom of the furnace, on a level with the lowest part of the hearth, one on each side corresponding to each pit; they are called "eyes" by the Germans, and are kept alternately closed and open. The pits in front have been fancifully compared to spectacles, whence the name "Brillenofen," or spectacle-furnace. The pressure of the

[9] De la Richesse Minérale, Heron de Villefosse. Paris, 1819, 3. p. 345 et seq.

blast is equal to that of a column of water from 8 to 10 inches in height.

The charge of the furnace is composed as follows:—*Roasted schist*, 2 Fuders (1 Fuder = 60 ctrs. = about 3 tons English), *fluor-spar* 8 ctrs., *concentration-slag* 6 ctrs., and any *residua* (Gekrätz) which may be at hand. The fuel is English coke at the rate of 5 *tons* measure (1 ton Prussian = 7 cub. feet Prussian) per Fuder: light coke weighs 150 lbs. and heavy coke 200 lbs. (Prussian) per ton. The products are ore-furnace regulus (Rohstein), containing from 30 to 35 per cent. of copper, and ore-furnace slag (Rohschlacke), which is stated not to contain more than from 2 to 5 loths of copper per ctr., *i. e.*, from 0·06 to 0·15 per cent. 3. The ore-furnace regulus is roasted in three-walled kilns, similar to those at Åtvidaberg previously described: after the first roasting, the contents of the kiln are turned over, broken up, and such pieces as require to be roasted a second time are put aside for that purpose; the greater part of the ore is usually roasted twice. It is hardly necessary to remark that care must be taken to leave sufficient sulphur in the roasted regulus to prevent the separation of metallic copper in the subsequent fusion. 4. The roasted regulus of No. 3 is smelted in a reverberatory furnace. The products are concentrated regulus (Spurstein), which is tapped into water and granulated as in the Welsh process, and slag which is skimmed off at once into small waggons and wheeled away. The charge is, 42 ctrs. of *roasted regulus*, of which from $\frac{1}{8}$ to $\frac{1}{4}$ has been only once roasted (one-fire Rohstein), and about 4 ctrs. of sand. It is introduced into the furnace in ladles through two doors, one at the end opposite the fire-bridge, and the other in the side opposite the tap-hole. The operation is conducted like the No. 4 fusion at Swansea. The slag is drawn out in from seven to eight hours, when a second charge of 42 ctrs. is introduced. The products are concentrated regulus (Spurstein) and concentration-slag: the regulus contains from 60 to 75 per cent. of copper, and amounts to about half the weight of the ore-furnace regulus. The average time required for the fusion of two charges of 42 ctrs. each, including charging, rabbling, tapping, &c., is about 19 hours. The fuel employed consists of equal parts of brown coal, which occurs in the neighbourhood, and English coal imported into Hamburgh. The regulus is stamped and ground, and in that state sent to the Gottesbelohnunghütte to be desilverized. At the Kreuzhütte there were four blast furnaces, and one reverberatory furnace.[9]

After the extraction of the silver from the regulus at the Gottesbelohnunghütte, the pulverulent residue in which the copper exists in the state of oxide is smelted. It is kneaded with from 5 to 10 per

[9] The ore-furnace slag is employed for domestic purposes as a source of heat. A lump of red-hot slag is taken off and a stick is thrust into it, when, owing to the evolution of gases from the wood, it swells out, forming a hollow ball. The stick is then pulled out, and the hole left is made large enough to receive a culinary pot. The lump of slag thus prepared is placed on two iron bars in a wheelbarrow, and taken away by women to the neighbouring huts. By this means vegetables are cooked, coffee is boiled, &c.; and in winter the rooms are heated by hot slag.

cent. of clay, and sufficient water to form a coherent mass, which is moulded by hand into balls from 3 to 4 inches in diameter. These are dried in hot chambers, and then smelted in a blast-furnace in admixture with ore-furnace slags, stamped quartz, and some thin-regulus; or failing this, some iron-pyrites free from silver may be added. It is essential that a certain amount of regulus should be present, in order that the slag may be as free from oxide of copper as possible. If a reverberatory furnace be employed, the cupriferous residue may, in admixture with carbonaceous matter, be smelted without the addition either of flux or regulus.[1]

Close to the Kreuzhütte are the new smelting works called Eckhardtshütte, which were on the point of completion in September, 1860. They are stated to be well lighted, more roomy, better ventilated, and in style much superior to the old establishments. There were four large blast-furnaces, of which two only were in blast, and two small ones; and a reverberatory furnace was in course of construction. The blast was produced by a fan worked by steam-power. The pressure was equal to a column of water of 4 inches in height, and the internal diameter of the nozzles of the blast-pipe was from $2\frac{1}{2}$ to 3 inches. At the Oberhütte the blast is obtained from a Cagniardelle, or machine constructed on the principle of the Archimedes screw: it is stated to produce a blast equal to a column of water 14 inches in height.

Analytical data in elucidation of the smelting of copper-schist in the district of Mansfeld:—

ANALYSES OF THE MANSFELD SCHIST BY BERTHIER.[2]

	1. Unburnt.		2. Roasted.	3. Roasted.
Silica	40·0	Silica	50·6	43·8
Alumina	10·7	Alumina } Magnesia }	23·4	17·2
Oxide of iron (Fe^2O^3)	5·0			
Carbonate of lime	19·5	Lime	7·8	18·0
,, magnesia	6·5	Oxide of copper (CuO)	2·8	2·5
Copper-pyrites	6·0	,, iron (Fe^2O^3)	9·0	7·2
Potash	2·0	Sulphur	4·0	2·4
Water and bitumen	10·3	Loss by calcination	0·8	6·0
	100·0		98·4	97·1

These analyses of three different specimens of the schist show that, as might be anticipated, it varies considerably in composition. Determinations of the silica, alumina, lime, magnesia, and oxide of iron in the schist from Sangerhausen and other localities in the district of Mansfeld have been made by Grunow,[3] and the results

[1] I am indebted for much of the preceding information to my former pupil, Mr. Foster, who visited the works Sept. 1860. I have also derived information from the MS. accompanying the collection of specimens from the Mansfeld Copper Works in the Great Exhibition of 1851, signed C. Th. Boettger, Eisleben, and from the work entitled Die Augustin'sche Silberextraction, by A. Grützner. Braunschweig, 1851, p. 91 et seq.

[2] Ann. des Mines, 1. s. 1824, v. 9, p. 63.

[3] Handb. der Metallurg. Hüttenkunde. Kerl, 1855, 2. p. 256.

agree pretty well with those inserted above. According to Berthier, the roasted schist melts very well without any addition in a brasqued crucible, forming a slag which is compact, vitreous, free from cavities, blackish, translucent, and very tenacious: shots of regulus are produced which are magnetic, and contain both copper and iron. The same metallurgist remarks that it is evident, from the proportion of sulphur in the 2nd and 3rd analyses, that the iron and copper are present in the roasted schist chiefly in the state of sulphides, and that, consequently, it is difficult to conceive the utility of the roasting process, of which the effect is the expulsion of the bituminous matter and a portion of the carbonic acid. Fresh analyses of this product are desirable.

ANALYSES OF ORE-FURNACE REGULUS (ROHSTEIN).

	1.[1]	2.	3.	4.	5.	6.
Copper	52·44	48·25	42·10	31·70	47·27	43·62
Iron	20·49	17·35	19·25	28·75	19·69	23·35
Sulphur	26·44	24·58	25·50	27·80	26·76	28·70
Zinc	..	2·90	5·20	4·35	..	3·45
Nickel, Cobalt	..	0·80	1·05	1·25	..	
Lead	0·41	1·05	1·50	0·65	..	..
Silver	0·13	0 30	0·27	0·16	..	..
Silica	..	1·55	1·15	1·65	Zn, Ni, Co, Mn 4·09	Carbon, earthy matter, and loss 0·88
	99·91	96·78	96·02	96·31	97·81	100·00

Observations.—1–4. By Heine. 1. The Rohstein was produced at Sangerhausen in 1831: the amount of copper was occasionally as low as 40 per cent., when the iron was proportionately increased. In addition to the constituents mentioned, traces of manganese, zinc, cobalt, nickel, antimony, and arsenic were found. The charge of the furnace consisted of 3 parts of a mixture of *dach*, *noberge*, and *sand-ore* to 5 parts of *copper-schist*, with the addition of from 10 to 20 per cent. of *fluor-spar* and *slags* from the concentration and black-copper furnaces. The fuel employed in smelting was charcoal. 2. From the Oberhütte, Eisleben. 3. From (the Katharinenhütte?) Mansfeld. 4. From the Kupferkammerhütte, Hettstädt. The last three analyses were made by Heine in 1844. The loss consisted of small quantities of alumina, lime, magnesia, molybdenum, phosphorus, &c. The silica, I presume, was simply in mechanical mixture. 5. By Rammelsberg. This Rohstein, of which the locality is not stated, was partially crystallized in octahedra of the cubical system, built one upon another: its sp. gr. was 4·73. 6. By Rammelsberg. This specimen was obtained in 1833 at the Katharinenhütte, Leimbach, from the lining of the hearth (Gestübemasse) into which the regulus had infiltrated in small

[1] Ann. der Phys. u. Chem. 1835, 34. p. 533. The other analyses are extracted from Rammelsberg's Lehrbuch der Chemischen Metallurgie. Berlin, 1850, pp. 224–226.

particles, and had afterwards crystallized during slow cooling. Crystals thus produced are more distinct than the last: they are combinations of the octahedron with the cube, having very smooth and brilliant faces, and sharply defined edges and angles; in colour they resemble kupfernickel, but sometimes are coated with a steel-grey tarnish.

A specimen of ore-furnace regulus in my possession produced at Mansfeld many years ago is coated with a blue and green efflorescence; its fracture is granular, and has a reddish iron-grey colour: it contains cavities near the upper surface, in some of which is moss-copper.

Analyses of Ore-furnace Slags.

	1.	2.	3.	4.	5.	6.
Silica	57·43	53·83	49·8	48·22	50·00	54·13
Alumina	7·83	4·43	12·2	16·35	15·67	10·53
Lime	23·40	33·10	19·2	19·29	20·29	19·41
Magnesia	0·87	1·67	2·4	3·23	4·37	1·79
Protoxide of iron	7·47	4·37	13·2	10·75	8·73	10·83
Oxide of zinc	..	..	..	1·26	1·11	..
Dioxide of copper	0·30	0·24	..	0·75	0·67	2·03
Fluor	1·97	2·09	1·1	..	..	..
Alkali (KO) and loss	..	..	2·1	..	..	..
	99·27	99·73	100·0	99·85	100·84	98·72

Observations.—1 and 2 from Sangerhausen, made by Heine in 1831.[5] No. 1 was pearl-grey, and so light and porous that it floated upon water like pumice. No. 2 was perfectly melted, glassy, and leek-green in colour. The difference between these two slags was attributed to the fact that in the production of the second a larger quantity of fluor-spar had been used than in the case of the first. 3. From Mansfeld, by Berthier,[6] who describes these slags as vitreous, translucent, and of a deep green, almost black, colour, occasionally tinted with blue. 4, 5, 6. From the Kupferkammerhütte. The analyses were made in Rammelsberg's laboratory,—the first two by Hoffmann, apparently with the same specimen, and the third by Ebbinghaus.[7] The slags were of the usual description, vitreous and dark-coloured.

Ore-furnace slags in my possession from Mansfeld and Sangerhausen are vitreous and olive-black when seen in mass; but viewed in thin pieces by transmitted light the colour is dark olive. Other specimens are partly vitreous and partly opaque and brown-grey; and others from Eisleben, which are reported to contain vanadium, are vitreous, and more or less blue, like slag occasionally produced in iron-smelting furnaces.

[5] Op. cit., p. 534.

[6] Ann. d. Mines, 1. s. 1824, 9, p. 66.

[7] Op. cit., p. 226.

ANALYSES OF CONCENTRATED-REGULUS (SPURSTEIN) AND THIN-REGULUS (DÜNNSTEIN) FROM THE BLACK-COPPER FURNACE.

Only the first analysis is of concentrated-regulus. The supposed rational constitution of these specimens of regulus, as calculated by Rammelsberg, is inserted below the ultimate analyses:—

	1.	2.	3.	4.	5.
Copper	51·37	59·8	59·18	57·27	61·23
Iron	18·67	15·8	16·07	16·32	15·19*
Sulphur	24·35	22·6	20·01	22·17	24·38
Zinc, nickel, &c.	6·54	..	2·97	2·55	..
	100·93	98·2	98·23	98·31	100·80
Disulphide of copper	67·47		46·66	57·69	77·95
Protosulphide of iron	24·75		25·11	25·56	23·80
Sulphides of zinc and nickel	..		4·44	3·81	..
Metallic copper	5·98		21·96	10·08	traces.

* With other metals.

Observations.—1. From the Kupferkammerhütte, by Ebbinghaus in Rammelsberg's laboratory. There is a deficiency of 2·48 of sulphur below what is required to form disulphide of copper, and protosulphides of iron and the other metals, so that Rammelsberg suggests that part of the iron exists as disulphide (Fe^2S). 2. From Mansfeld, by Berthier.[8] 3, 4, 5. These specimens of thin-regulus were analysed in Rammelsberg's laboratory by De la Trobe, Schliesser, and Boujoukas respectively. Rammelsberg states that this regulus always contains moss-copper, not only in cavities, but also in its compact substance.

A specimen of *Spurstein* in my collection from Mansfeld is ¾ inch thick: it contains numerous elongated tube-like cavities, perpendicular to the unfractured surfaces; many of these cavities contain teeth-like projections of metallic copper; the colour of a fresh fracture is dark grey, like disulphide of copper, with a distinct reddish tinge. A specimen of *Dünnstein* from Mansfeld is ¼ inch thick: its surfaces are parallel; it is full of tube-like cavities, many of which contain projecting teeth of metallic copper; the colour of a fresh fracture is grey, like disulphide of copper; there is no efflorescence upon the surface. A specimen from Sangerhausen is pimpled on the surface exactly like *pimple-metal*; it is compact, and not porous like the last; the colour of its fracture is grey, like disulphide of copper; particles of metallic copper are thinly disseminated through the mass.

ANALYSES OF SLAGS ACCOMPANYING CONCENTRATED-REGULUS (SPURSCHLACKE) AND BLACK-COPPER.

	1.	2.	3.	4.	5.
Silica	33·18	34·11	33·6	38·15	37·90
Alumina	11·22	8·46	5·6	..	..
Protoxide of iron	32·03	37·68	51·5	47·22	49·23
Lime	17·14	13·38	5·0	11·56	9·07
Magnesia	2·96	4·57	..	0·03	1·47
Copper existing partially as disulphide	1·90	0·68	Cu^2O 3·0	2·86	1·59
Sulphur	not determ.	0·46	..	..	..
	98·43	99·34	98·7	99·82	99·26

[8] Ann. d. Mines, 1. s. 9. p. 68.

Observations.—1, 2. Slags accompanying the formation of concentrated-regulus; the analyses were made in Rammelsberg's laboratory by Wornum and Hoffmann respectively. The slags are described as more stony than glassy, bluish black, slightly shining or dull. They are decomposable by hydrochloric acid. In each analysis the oxygen of the silica is equal to that of all the bases (17·25 : 18·96 in the first, and 17·72 : 17·90 in the second); these slags are, therefore, tribasic or singulo-silicates. 3. Black-copper slag from Mansfeld, by Berthier, who describes it as compact, heavy, black, and magnetic, resembling certain slags produced in the conversion of pig-iron into malleable iron.[0] 4, 5. Black-copper slags. The analyses were made in Rammelsberg's laboratory by Lade and Gehrenbeck respectively. They are described as stony, black, and decomposable by hydrochloric acid. The oxygen of the silica is equal to that of the bases; so that, like the slags accompanying concentrated-regulus, they are tribasic or singulo-silicates.[1]

ANALYSES OF THE COMPLETELY-ROASTED REGULUS (GAARROST).

	1.	2.
Copper	51·97	67·59
Iron	20·39	10·56
Zinc and nickel	..	0·67
Oxygen	13·61	8·67
Sulphur	2·11	1·64
Matter insoluble in acids	11·92	9·49
	100·00	98·62

Observations.—These analyses were made in Rammelsberg's laboratory. The insoluble matter contained silica and protoxide of copper. From the preceding results it may be concluded that the roasted regulus consists chiefly of dioxide of copper and magnetic oxide of iron (Fe^3O^4).

A specimen of six times roasted regulus in my collection (Spurgaarrost) from Sangerhausen is a heavy, imperfectly melted mass, containing lumps of metallic copper; it is brown-red, and appears to contain a large quantity of dioxide of copper; when seen under certain conditions of incident light, the characteristic ruby colour of laminæ of fused dioxide of copper may be distinctly perceived on its surface.

ANALYSES OF BLACK-COPPER.

	1.	2.	3.
Copper	95·45	89·13	92·83
Iron	3·50	4·23	1·38
Lead	..	0·97	2·79
Silver	0·49	not determ.	0·26
Zinc, nickel, and cobalt	..	3·98	1·05
Sulphur	0 56	1·07	1·07
	100·00	99·38	99·38

Observations.—1. By Berthier. No trace either of nickel or cobalt was found.[2] 2 and 3. By Hoffmann and Ebbinghaus respectively, in

[0] Ann. d. Mines, loc. cit. [1] Rammelsberg, op. cit. [2] Op. cit., p. 68.

Rammelsberg's laboratory. The percentage of silver in No. 3 corresponds to 84 ozs. 18 dwts. 15 gr. per ton of 2240 lbs.

Analyses of the "bear" (Eisensau).

In the vicinity of Magdeburg in 1831 several lumps of iron-like metal were discovered in the ground, about 4 feet below the surface; and as no iron-works had existed in the locality, it was suspected that they were of meteoric origin. They were analysed by Stromeyer, who found them to consist chiefly of iron, and to contain a considerable quantity of molybdenum, a metal of very unusual occurrence, and not previously known as a constituent either of meteoric iron, or of any furnace product. The metal was hard, and when in small pieces could be broken as easily as white cast-iron, and reduced to coarse powder in a mortar. A freshly-fractured surface was scaly-granular (schuppig-körniges), had a tolerably bright lustre, and a tin-white colour passing into grey. On examining different pieces, two varieties of metal were observed: one was distinctly scaly, more coarsely granular on fracture, and had a greyer colour; the other was indistinctly scaly and more finely granular on fracture, somewhat lighter in colour, and more brittle. The sp. gr. of the coarse-grained variety was 7·2182, and that of the fine-grained 7·3894. In intimate admixture with the ferruginous mass, especially in the coarse-grained variety, was a large quantity of a metallic sulphide, which in appearance and other respects resembled purple copper ore ($3Cu^2S+Fe^2S^3$). This sulphide occurred chiefly towards the exterior, and in places constituted almost entirely the outer layer of the mass. In the interior of some of the pieces extremely small quantities of moss-copper were found.[3] Heine subsequently analysed "bears" from the Oberhütte at Eisleben, and ascertained that their composition was identical with that of the metallic lumps discovered at Magdeburg. He published an elaborate paper on the subject in 1836.[4] Both varieties of metal are soluble in hydrochloric and nitric acids; and at first metallic scales are separated, which dissolve more slowly than the rest of the mass.

	1.	2.	3.	4.	5.
Iron	76·77	74·60	73·26	57·68	57·91
Molybdenum	9·97	10·19	9·13	27·33	28·49
Copper	3·40	4·32	1·79	2·49	2·45
Cobalt	3·25	3·07	0·77	5·50	0·67
Nickel	1·15	1·28	4·63		3·42
Manganese	0·02	0·01	..	..	..
Arsenic	1·40	2·47	..	..	..
Phosphorus	1·25	2·27	6·04	4·58	3·51
Sulphur	2·06	0·92	0·09	0·46	0·60
Silicon	0·35	0·39	..	..	..
Carbon	0·38	0·48	1·42	1·31	0·87
	100·00	100·00	97 13	99·35	97·92

Observations.—1, 2. From Magdeburg, by Stromeyer: No. 1 coarse-

[3] Ann. d. Phys. u. Chem. Poggendorff, 1833, 28. p. 551.

[4] Jour. fur prakt. Chem. Erdmann. 1836, 9. p. 177.

grained, No. 2 fine-grained variety. 3, 4, 5. From Eisleben, by Heine: No. 3 coarse-grained, sp. gr. 7·578; Nos. 2 and 3 fine-grained, sp. gr. 7·578. According to Heine, Augustin was the first to suggest that in this interesting product the function of molybdenum might be regarded as analogous to that of arsenic in *speise*. The processes employed in all these analyses appear to be defective in certain respects.

Rammelsberg has published the following analysis of a remarkable product from the Mansfeld smelting-works: its mode of formation is not known; it is in imperfectly defined prismatic crystals, which are partially coated on the surface with sulphate of copper; they are magnetic, and their fracture is silver-white passing into grey, granular and shining.[5]

Iron	63·23
Copper	12·69
Cobalt with traces of nickel	8·22
Molybdenum	8·40
Sulphur	9·43
	101·97

Black-vitriol.—The rich regulus was washed with water several times during the process of roasting, and the solution of sulphate of copper was evaporated, in order to obtain the salt in crystals. The mother-liquor was added to the solution obtained in a subsequent washing of regulus, and the mixed liquors were evaporated, and set to crystallize. The second mother-liquor was again evaporated in admixture with fresh solution; and this was again repeated. At last there remained a dark-coloured mother-liquor (Schwarzlauge), from which crystals of *black-vitriol* were produced. They have the form of green-copperas or sulphate of protoxide of iron, are bluish-black in colour, and are often of considerable size. The salt, according to Rammelsberg, contains magnesia and protoxides of copper, iron, manganese, cobalt and nickel;[6] and, as its form would indicate, 7 equivalents of water. A specimen in my collection contains so much cobalt, that after the precipitation of the copper by sulphuretted hydrogen, the solution has a tolerably deep red colour.

Intermixed with the crystals of black-vitriol, others of a pale bluish-green colour are occasionally found, which, according to Rammelsberg, have the following composition:—

		Oxygen.
Sulphuric acid	35·56	21·30
Protoxide of copper	4·47	
Iron	0·52	
Oxide of zinc, protoxide of nickel, with some cobalt and manganese	15·27	4·31
Magnesia	0·63	
Potass	18·39	3·12
Water	25·16	22·37
	100·00	

The composition of the salt may be expressed by the formula

[5] Lehrb., p. 229. [6] Ib., p. 231.

$(RO,SO^3+KO,SO^3)+6HO$: and it is similar in form to the analogous double salts of potass and ammonia.[7] It is remarkable that the potass derived from the ore and the ashes of the fuel should thus become concentrated in this salt.

Crystals of artificial felspar.—Heine was the first to analyse and describe this interesting product, which was met with for the first time at Sangerhausen in 1834, during the reparation of one of the blast (ore) furnaces.[8] It occurred in well-defined white and pale-violet crystals, which were attached to the back wall in a space included between 1. and 2½ feet above the twyers, and were disclosed after the removal of an incrustation consisting chiefly of blende, from this part of the interior of the furnace. Similar crystals existed in fissures and holes in the stone-work, and also upon a carbonaceous coating which firmly adhered in thin layers to the sides of the hearth, and was not unlike graphite in appearance, except that it was deeper in colour: the stones used in the construction of the shaft and hearth of the furnace were quartz conglomerate. Besides the crystals, there was found in the furnace incrustation a compact spar-like substance, having a conchoidal fracture, but in colour and other characters resembling the crystals. I have several specimens of these crystals from the Sangerhausen furnace. Some are perfectly colourless, others have a delicate amethystine tint, and others again appear almost black, possibly from the presence of intermixed carbon or dark blende: they vary considerably in size, one of the largest rhombic faces being $\frac{3}{16}$ths of an inch in width; they scratch glass, and, according to Heine, their sp. gr. is 2·56; they have generally the form of adularia. Crystals of the same kind of felspar have also been found in furnaces at Leimbach.

ANALYSES.

	1.	2.	3.	4.
Silica	64·53	65·95	65·03	63·96
Alumina	19·20	18·50	16·84	20·04
Sesquioxide of iron	1·20	0·69	0·88	
Lime	1·33	4·28	0·34	0·43
Magnesia	..	..	0·34	0·54
Protoxide of copper	0·27	0·13	0 30	..
Sesquioxide of manganese (Mn^2O^3)	..	..	0·36	..
Oxide of zinc	traces	traces	..	..
,, cobalt				
Potass	13·47	10·47	15·26	12·49
Soda	..	..	0·65	0·65
	100·00	100 02	100·00	98·11

Observations.—1 and 2. By Heine: 1, by fusion with carbonate of soda; 2, by fusion with carbonate of baryta: in both analyses the potass was estimated by loss, and the presence of a little soda was considered probable. 3. From Sangerhausen, by Abich.[9] Sp. gr.

[7] Lehrb., p. 231.

[8] Annal. d. Phys. u. Chem. Poggendorff, 1835, 34. p. 531. Ueber künstliche Feldspathbildung. Von Bergprobirer Heine in Eisleben.

[9] Geolog. Beobacht. Braunschweig, 1841, p. 10.

2·56. The silica contained a trace of titanic acid. The analysis was made by means of hydrofluoric acid. Abich suggests that the amount of lime in No. 3 is erroneous, and that the error was, probably, occasioned by the presence of baryta. The crystals selected for analysis by Abich were perfectly pure, and of a pale amethyst colour. 4. By Rammelsberg. These crystals were obtained from smelting-works at Leimbach: they were vitreous in lustre, grey, and had the sp. gr. of 2·665.[1] From the preceding analyses may be deduced the formula $KO,SiO^3 + Al^2O^3,3SiO^3$, which is that of orthoclase.

Smelting of Copper-schist at Riechelsdorf in Hesse.

Copper-schist occurs here in the same geological position as in the province of Mansfeld, and has long been smelted: it is not sufficiently argentiferous for the profitable extraction of the silver. The products of smelting at the Friedrichshütte, Riechelsdorf, have been analysed by Genth, under the direction of Bunsen; and of all the analyses which have been published in elucidation of the chemistry of copper-smelting, few appear to be so complete, or more worthy of confidence.[2]

The Noberge and Unterschiefer (Letten) of the bed of schist and the underlying sand-ore were smelted at these works: the schist generally contains not more than from 2 to 3 per cent. of copper, and the sand-ore from 3 to 4 per cent., rarely from 6 to 7 per cent. Purple copper-ore and iron-pyrites are the chief metallic constituents; in addition to these and disseminated through the ore occur copper-pyrites, red copper-ore, vitreous-copper-ore, blue and green carbonate of copper, native copper, kupfernickel, smaltine (tin-white cobalt, Speis-kobalt), zinc-blende, galena, molybdenite (sulphide of molybdenum), grey-copper (Fahlerz), and others.

The process of smelting consisted of the following operations:—1. Roasting the schist in large open heaps. 2. Fusion of the roasted schist with black-copper slags in a blast-furnace with two receivers in front (Brillenofen). On the bottom of the hearth a ferriferous "bear" (Eisensau) was formed as usual; on the top of this was regulus, covered with slag, which, according to its different modifications, received the names of raw-slag, Schwiel, and Schwiel-slag. In addition to these ordinary products of ore-smelting, others of much interest in a scientific point of view were occasionally formed. Thus on the front wall of the blast-furnace and in the cooler parts sulphur, realgar, arsenious acid, blende, galena, &c., have been found sublimed. 3. The regulus from the last operation was roasted nine or ten times successively; the product was mixed with charcoal and ore-furnace slag, and smelted in a low blast-furnace (Krummofen), when black-copper and thin-regulus (Dünnstein) were obtained. This regulus was added to the ore-furnace regulus in the 4th or 5th fire, and roasted. 4. The

[1] Lehrb. d. Chem. Met. 233.

[2] Chemische Untersuchung der beim Kupferschiefer-hüttenprocess fallenden Producte. Jour. f. prakt. Chem. 1846, 37. p. 193 et seq. Genth was assistant of Bunsen at Marburg. This investigation has also been published in the Berg. u. hüttenm. Zeit. 1846, p. 617 et seq.

black-copper was refined in the common refining-hearth (Gaarheerd); the products were as usual rosette-copper and refinery-slag, or skimmings (Gaarkrätze). The following analyses of the products were all by Genth:—

ANALYSES OF REGULUS.

	1. Ore-furnace regulus.	2. Ore-furnace regulus.	3. Black-copper or thin-regulus.
Copper	42·95	43·81	61·26
Silver	..	0·09	..
Lead	1·21	0·87	..
Iron	27·08	24·96	13·70
Nickel	0·57	1·14	traces
Cobalt	trace	trace	4·11
Manganese	..	2·33	traces
Calcium	0·44	0·96	do.
Sulphur	28·29	26·57	22·51
	100·54	100·73	101·58

Observations.—1. From a disc taken at the upper part of one of the receiving cavities. Crystalline-granular, fracture uneven, somewhat inclined to splintery, opaque, lustre metallic, colour of a fresh fracture pale bronze-yellow (Speisgelb), but after a few seconds acquiring a tint of copper-red and indigo-blue, sp. gr. 5·223; soluble in nitric acid; full of cavities containing fine capillary metallic copper; the magnet extracts from the finely-pounded regulus a sulphide of iron of the colour of magnetic pyrites. According to Genth the constitution of this regulus may be expressed as follows:—

Sulphide of lead	1·40	containing of sulphur		0·19
Magnetic pyrites (Fe^7S^8)	44·84	,,	,,	17·76
Sulphide of nickel (NiS)	0·88	,,	,,	0·31
Disulphide of copper	49·57	,,	,,	10·03
Metallic copper	3·41	,,	,,	..
	100·10			28·29

The composition of magnetic pyrites may be equally well expressed by either of the two formulæ—$5FeS,Fe^2S^3$ and $6FeS,FeS^2$. 2. The regulus was from the lowest part of one of the receiving cavities (Kupfersteinkönig). In external characters it was precisely similar to the last; sp. gr. 5·147. According to Genth its constitution may be expressed as follows:—

Silver	0·09			
Sulphide of lead	1·00	containing of sulphur		0·13
Magnetic pyrites	41·33	,,	,,	16·37
Sulphide of nickel	1·76	,,	,,	0·62
,, manganese (MnS)	3·68	,,	,,	1·35
Disulphide of copper	40·03	,,	,,	8·10
Metallic copper	11·88			
	99·77			26·57

3. In thin crystalline plates. It is stated that in "physical characters" it was similar to ore-furnace regulus; but its colour must

certainly have been different; sp. gr. 5·004; its surface consisted of a thin coating of metallic copper. Its constitution may be expressed by the formula $R^2S,3Cu^2S$, in which $R^2 = Fe\frac{2}{3} + Co\frac{1}{3}$. Calculated from this formula, its composition is as follows:—

Iron	14·40
Cobalt	3·80
Copper	61·13
Sulphur	20·67
	100·00

The sulphur found is 1·84 in excess of that deduced by calculation; and this Genth attributes to his neglect in the analysis to treat the sulphate of baryta after ignition with hydrochloric acid.

ANALYSES OF SLAGS.

	1. Ore-furnace slag.	2. Red-brown ore-furnace slag.	3. Ore-furnace slag, by the addition of sand-ore.	4. Schwiel.	5. Black-copper slag.	6. Refinery Slag.	7. Slag from refined copper.
Silica	48·23	44·47	51 41	45·41	31·72	7·88	32·23
Alumina	6·51	12·96	19·32	18·11	2·83	0·81	5·60
Protoxide of copper	0·58	1·23*	..	0·30	1·07	1·26	4·79
,, molybdenum (MO)	trace	0·38	..	0·25	0·23	2·36	0·87
,, iron	14·13	7·85	5·88	6·31	47·80	82·49	20·72
,, cobalt	trace	trace	..	..	0·25	trace	trace
,, nickel	do.	do.	..	..	trace	3 59	34·16
,, manganese	0·65	0·30	0·89	0·84	do.	..	..
Magnesia	3·35	7·00	1·40	7·15	3·86	..	trace
Lime	23·06	21·20	17·80	18·49	8·06	1·70	do.
Potass	3·75	2·90	1·78	3·09	3·68	0·31	1·23
Soda	0·88	0·87	0·65	0·70	1·26	0·25	0·43
Protosulphide of copper (CuS)	..	..	0·67	..	..	..	..
Tersulphide of molybdenum (MS^3)	..	..	0·20	..	..	..	..
Protosulphide of iron (FeS)	..	..	1·40	..	..	..	..
	101·14	99·16	101·43	100·65	100·76	100·65	100·03

* Cu^2O.

Observations on the characters of the preceding slags.—1. Amorphous, fracture conchoidal and splintery, lustre vitreous or waxy, colour between pitch- and velvet-black, streak greyish-white, opaque, in thin splinters translucent, and greenish-grey by transmitted light, sp. gr. 2·834; readily soluble in hydrochloric acid with the separation of gelatinous silica. The composition of this slag may be expressed by the formula $24(3RO,2SiO^2) + 2Al^2O^3,SiO^3$. 2. Streaked with red-brown veins, sp. gr. 2·683, in other respects resembling the last. The composition of this slag may be expressed by the formula $3(2RO,SiO^3) + Al^2O^3,SiO^3$. 3. Similar to the ordinary ore-furnace slag, sp. gr. 2·731, more or less vesicular. The composition of this slag may be expressed by the

(very improbable?) formula $10(3RO,2SiO^2)+3(4Al^2O^3,5SiO^2)$. 4. Crystalline-granular, fracture uneven and splintery, opaque, translucent at the edges, pearly vitreous lustre, colour between ash-grey and greenish-grey, streak greyish white, sp. gr. 3·023; not completely decomposable by hydrochloric acid. Schwiel is an impure slaggy mass, which collects round the edges of the receiving vessels in front of the furnace; it contains much intermixed regulus, and is melted over again. Its composition may be expressed by the formula $9(2RO,SiO^2)+5Al^2O^3,SiO^2$, or by the (not less improbable?) formula $6(3RO,2SiO^2)+5Al^2O^3,2SiO^2$. Partial analyses of three varieties of Schwiel slag were made, but the composition was found to be so variable that it was not considered worth while to complete them. The proportion of silica varied from 48·44 to 58·28 per cent., and that of the lime from 18·50 to 22·27 per cent. 5. Crystalline, in the form of sheets, with a wrinkled surface, structure granular and in part finely radiating, opaque, lustre vitreous inclining to metallic, colour between bluish- and velvet-black, streak grey, sp. gr. 3·512, magnetic; decomposable by hydrochloric acid. The composition of this slag may be expressed by the formula $36(3RO,SiO^2)+3Al^2O^3,2SiO^2$. 6. Knobby, vesicular, fracture uneven and crystalline, opaque, lustre between vitreous and metallic, colour iron-black, streak grey, sp. gr. 4·609, strongly magnetic; not soluble in hydrochloric acid; the cavities are in part filled with shots of metallic copper and an almost silver-white alloy of copper and nickel. 7. Small black slaggy particles, which in appearance exactly resemble the Lapilli from Vesuvius, sp. gr. 4·135, magnetic. It is not stated how this slag was produced: was it obtained in the remelting of refined copper in the process of toughening (Hammergaarmachen)? Its composition may be expressed by the formula $5(3RO,SiO^2)+Al^2O^3,SiO^2$.

ANALYSES OF COPPER.

	1. Black copper.	2. Black copper.	3. Refined copper.	4. Tough copper.	5. Refined copper residue.
Copper	83·29	92·24	83·90	99·31	98·97
Silver	0·059	0·10	do.	0·10	0·13
Lead	0·31	0·89	0·60	0·21	0·07
Iron	1·66	1·41	..	0·02	0·23
Cobalt	traces	traces	..	..	..
Nickel	3·28	4·15	1·10	0·28	0·27
Protoxide of nickel	..	..	13·86	traces	..
Calcium	0·05	0·13	0·10	0·03	0·04
Magnesium	0·01	traces	0·12	0·01	traces
Potassium	0·03	0·10	0 32	0·04	0·07
Aluminium	traces	..	..	..	..
Sulphur	11·31	0·98	traces	traces	traces
Slag	..	..	do.	do.	0·22
	100·00	100·00	100·00	100·00	100·00

Observations.—In all these analyses, not less than from 15 to 20

grammes were operated on in each analysis: the weight of the copper was deduced indirectly, by subtracting the sum of the weights of all the other ingredients from the weight of metal taken for analysis. 1. Upper disc. Crystalline with indented surface (zähniger Oberfläche), very finely granular, fracture hackly, opaque, lustre perfectly metallic, copper-red and silver-white, tarnished black; sp. gr. of a disc from the middle, 7·305. 2. From the lump of copper remaining after the discs have been all taken off (Kupferkönig). Knobby, vesicular, in other respects similar in external characters to the last. 3. Uppermost disc. A plate-like mass, consisting of numerous thin layers of metallic copper cohering together, over which are disseminated small black octahedra of protoxide of nickel; crystalline, pulverisable, fracture hackly, colour between black-grey and copper-red. By the action of nitric acid is obtained an insoluble residue, which consists of minute crystals of pure protoxide of nickel mixed with some slag. These crystals are octahedra, belonging to the cubical system; they appear black by reflected, and ruby-red by transmitted, light; they are completely insoluble in concentrated sulphuric, nitric, hydrochloric, and nitro-hydrochloric acids. They undergo no change whatever in melted carbonate of soda; but when heated to redness with bisulphate of potash, a double sulphate of potash and protoxide of nickel is formed. When heated in hydrogen they are reduced to the metallic state.[3] The production of these crystals in the refining process is a very interesting fact. I have had an opportunity of examining a specimen of them, with which I was favoured by Genth many years ago. It seems rather remarkable that potassium, calcium, and magnesium should exist in melted copper, which must certainly have contained dioxide of copper, and through which oxide of nickel is copiously disseminated. Moreover, the proportion of these metals in refined copper is much greater than in black-copper, notwithstanding the powerfully oxidizing influence to which the latter is subjected during the process of refining. It would even appear from the analyses that the whole of the iron and the greater part of the nickel may be removed from black-copper by oxidation, without any sensible reduction in the proportion of such extremely oxidizable metals as those of the potassium and calcium groups. 4. Thick disc of tough copper (Hammerkupfer), tough, but not "Hammergaarkupfer." Colour pure copper-red; innumerable small channels, through which gas had escaped, traversed the metal from the lower to the upper surface, and communicated especially to this disc "a decidedly radiated, crystalline-granular fracture." 5. From the lump of copper (Gaarkupferkönig) after the discs of copper had been all taken off. Vesicular, crystalline-granular, radiated fracture.

It was ascertained by Genth that in the melting and refining of black-copper the silver did not become concentrated in any particular part of the copper, so that it could be profitably extracted. In the

[3] Jahres-Bericht. Berzelius, 1846, v. 25, p. 170.

black and refined copper of the Friedrichshütte the proportion of silver in the centner varies from 2·to 3 loths,—that is, from about 20 to 30 ozs. per ton: discs were successively taken off during the course of one operation of refining, and were found to contain the following proportions of silver:—

	Contained of silver per cent.		Contained of silver per cent.
Upper discs of black-copper	0·059	First thin disc of refined copper	0·059
Middle do. do.	0·049	Second do. do.	0·066
König do. do.	0·104	Third do. do.	0·105
Uppermost disc of refined copper	traces	Fourth do. do.	0·067
Second do. do.	0·058	Fifth do. do.	0·066
When tough (Hammerkupfer) do.	0·101	Gaarkupferkönig do.	0·132

Genth made the three following analyses of "Hammergaar" copper from Dillenburg, in Nassau:—

	1. Uppermost disc.	2. Middle disc.	3. Residue, or König.
Silver	0·056	0·056	trace
Lead	..	0·038	0·069
Iron	traces	0·107	0·015
Copper	99·944	99·799	99·916
Residue	..	..	traces
	100·000	100·000	100·000

ANALYSES OF THE "BEAR" (EISENSAU).

	1.	2.
Phosphorus	1·04	0 04
Arsenic	..	traces
Carbon	0·73	1·12
Sulphur	0·59	0·31
Silicon	2·98	1 28
Aluminium	traces	traces
Iron	86·64	84·24
Manganese	..	traces
Nickel	traces	
Cobalt	3·61	2·85
Molybdenum	..	6·98
Copper	5·19	4·52
	100·78	101·34

Observations.—1. From the hearth-bottom of the furnace. Crystalline, coarsely-granular, fracture uneven, opaque, lustre metallic, colour steel-grey, brittle, sp. gr. 7·466, hardness = 5·5 (between apatite and felspar); it contains a few cavities, in which are small octahedra of metallic iron "united in toothed knitted masses," but very little moss-copper; here and there were small round grains of a crystallized black-blue compound, of which the quantity was too small for investigation. 2. This "bear" was from one of the receiving cavities (Brillheerd). Crystalline, finely granular, fracture uneven, opaque, lustre metallic, colour between steel-grey and tin-white, brittle, sp. gr. 7·549, hardness the same as that of the last; soluble in hydrochloric acid.

Other accessory Products.

Zinc-blende.—It occurs in crystalline masses, foliated, occasionally composed of radiating fibres; opaque, fracture uneven or splintery, lustre adamantine and metallic, colour between smoke-grey and greyish-black, streak greenish-grey, sp. gr. 3·784, hardness = 3 (calc-spar); soluble in nitric acid; it is occasionally tarnished of a golden-yellow colour; it is not abundant. Genth has given the following analysis of a specimen:—

Analysis.		Supposed constitution.		Containing of sulphur.
Zinc	57·51	Sulphide of zinc	85·91	28·40
Manganese	0·55	,, manganese	0·86	0·31
Iron	4·08	,, iron (FeS)	6·42	2·34
Copper	1·06	Disulphide of copper	1·33	0·27
Lead	2·79	Sulphide of lead	3·22	0·43
Molybdenum	0·15	,, molybdenum (MS^4)	0·30	0·15
Calcium	1·06		1·06	..
Sulphur	31·89			31·90
	99·09			

The state of combination of the calcium is regarded as doubtful; but there is no difficulty in understanding how it should be present as sulphide, and how this sulphide should be combined with other sulphides.

Sulphur.—It has been found in crystals, which in colour and lustre were precisely similar to those of native sulphur.

Arsenious acid.—It occurs in octahedrons and tetrahedrons up to 0^{mm}6 (nearly $\frac{1}{4}$ in.) in diameter, generally with step-like depressions, opaque, and having an adamantine lustre.

Realgar.—It had only once been met with at these smelting-works (1846), in pieces of a magnificent aurora red colour, and having a crystalline, foliated structure. I have a beautiful specimen of this substance from a roast-heap at Freiberg.

Galena.—It exactly resembles native galena, and presents distinct laminations parallel to the faces of the cube.

Fume.—It was in the state of dry powder, of a yellowish-white colour inclining to grey. It was *partly soluble in water*: the aqueous solution contained sulphates of protoxide of copper, sesquioxide of iron, protoxide of manganese, oxide of zinc, alumina, lime, magnesia, and potash, chloride of sodium and arsenious acid. The *insoluble residue* was boiled with hydrochloric acid: the solution contained the following substances—sulphuric acid, oxide of lead, oxide of zinc, sesquioxide of iron, arsenious acid, oxide of antimony, lime, protoxide of nickel, magnesia, potass, soda, molybdic acid, oxide of bismuth, and organic matter. The *residue insoluble in hydrochloric acid* consisted of sulphate of lead and combinations of silica: the following bases were also present, sesquioxide of iron, alumina, lime, magnesia, potass, soda, oxide of zinc, protoxide of copper, and traces of oxide of bismuth and protoxides of manganese and nickel.

Copper-smelting in Perm, in Russia.[4]

According to Gustave Rose the ores of copper occur in the "Weissliegende" of German geologists. The sandstone of the country, which consists chiefly of grains of quartz and fragments of other hard rocks cemented together by a marly substance, is more or less impregnated with chrysocolla and blue carbonate of copper. In the lines of stratification are found malachite, small crystals of blue carbonate of copper, vanadiate of copper, and, rarely, vitreous-copper, copper-pyrites and iron-pyrites. Native copper is also present. Upon the sandstone is a dark-coloured bituminous massive or schistose clay, which contains disseminated globules of vitreous-copper and subordinate beds of copper-pyrites (strates subordonnées de pyrite cuivreuse). Blue and green carbonates of copper are generally found in the lines of stratification. The ores were smelted with the addition of 30 per cent. of dolomite. The average produce of copper might be estimated at 2½ per cent. The fuel was charcoal. The smelting was effected in blast-furnaces having one twyer each and a fore-hearth like the Åtvidaberg furnaces. The chief dimensions were as follow:—height of the shaft 4^m 44 (14 ft. 7 in.); diameter of the mouth 0^m 62 (2 ft.); the belly was 1^m 07 (3 ft. 6 in.) wide by 1^m 24 (3 ft. 13 in.); the hearth 1^m 07 (3 ft. 6 in.) broad by 0^m 62 (2 ft.), and 0^m 71 (2 ft. 4 in.) deep; the fore-hearth was semi-elliptical, the long axis being 0^m 31 (1 ft.), the short axis 0^m 26 (10 in.), and the depth 0^m 33 (13 in.). The quantity of ore smelted daily varied from 3684 to 4502 kilogrammes (*i. e.* in round numbers from 3¾ to 4½ tons). The products were slag, *cupriferous pig-iron*, and black-copper. The metallic products were tapped out once in 24 hours. The pig-iron formed the upper stratum, and was first removed in discs or round cakes, after which the black-copper was removed in a similar way.

Choubine has given the following analyses of two varieties of cupriferous sandstone.

	1.	2.
Protoxide of copper	23·08	2·50
Vanadic acid (VO^3)	..	0·53
Silica	34·91	53·15
Alumina	3·46	5·24
Sesquioxide of iron	1·23	4·19
Protoxide of iron	0·23	0·39
Oxide of manganese	traces	traces
Lime	5·87	8·94
Magnesia	4·09	5·77
Potass	0·38	0·84
Sulphur	0·13	0·59
Bituminous matter	4·47	3·09
Carbonic acid	12·66	9·33
Water	7·08	2·90
	97·59	97·46

[4] Coup d'œil sur le travail de Cuivre aux Usines de Perm (called Jougovsk and Motovilikhinsk); par M. le Lieutenant Choubine. Annuaire du Journal des Mines de Russie. Année 1842. S. Pétersbourg, 1845, p. 184 et seq. See also the same work, Année 1840, p. 250. Notice sur les produits de la fonte des

It is stated that, in general, the slags were very good, and that the oxygen of the silica was double that of the bases. They varied in sp. gr. from 2·31 to 2·78. The black copper contained on an average 90 per cent. of copper; its sp. gr. varied, according to the proportion of iron present, from 7·811 to 8·097. One specimen analysed by Choubine is reported to have had the following composition :—

Copper	90·52
Iron	6·17
Vanadium	1·21
Carbon	0·94
	98 84

There was, probably, a considerable error in the determination of the carbon in this analysis, for, admitting the iron to have been combined with the maximum of carbon (about 5 per cent.), it would follow that not less than 0·615 of carbon must have been combined with the copper and vanadium, a conclusion which is entirely opposed to the results of other observers.

The *cupriferous pig-iron* is a remarkable product. A specimen, of which the analysis by Choubine is inserted below, was white, granular in structure, and even in fracture; it was extremely hard, and easily scratched glass; its sp. gr. was 7·432; particles, or small grains, of metallic copper were seen disseminated on its fractured surface. It was conjectured that its great hardness might be due to the presence of vanadium.

CUPRIFEROUS PIG-IRON.

Iron	75·97
Copper	12·64
Vanadium	1·99
Aluminium	0·89
Calcium	0·95
Magnesium	0·78
Silicon	2·51
Carbon	3·03
	98·76

The discs of cupriferous pig-iron were interstratified with charcoal, and melted in a refining-hearth (Gaarheerd), lined with a mixture of clay and sand. The products were black-copper and a slag of silicate of protoxide of iron, which, being very fusible, ran off; the silica was supplied by the coating of the hearth and the silicon contained in the metal. The sp. gr. of this slag was 4·070, and its composition was as follows :—

Silica	18·15
Vanadic acid	1·57
Alumina	0·36
Protoxide of iron	75·50
,, copper (Cu^2O ?)	0·40
Lime	1·97
Magnesia	1·03
	98·98

Minérais de Cuivre aux Usines de Perm, by the same author. Some of the analyses differ considerably from those of similar products in the subsequent communication above referred to. There is also another paper by the same author, Année 1841, p. 319, containing the details of the analyses which I have inserted.

The formula approximates to $6FeO,SiO^2$.

The copper present in this slag was in the form of metallic shots. In one refining-hearth 491 kil. (1082·6 lbs.) of cupriferous pig-iron were worked off in the course of twelve hours, by which 73kil.·5 (162 lbs.) of black-copper and 564kil.·9 (1245·6 lbs.) of slag were produced.

If this slag contained ½ per cent. of copper, it was melted in the ore-furnace in conjunction with unclean slags, ore-furnace slag, and refinery-slag, when two products were obtained—slag, and a cupriferous "bear" (loupe cuivreuse). The slag had the sp. gr. 3·271, and was composed as follows :—

Silica	31·61
Vanadic acid	1·30
Alumina	1·48
Protoxide of iron	57·00
,, copper (Cu^2O ?)	0·91
Lime	4·24
Magnesia	1·58
	98·12

The formula approximates closely to $3RO,SiO^2$. It will be observed that this slag contains more than ½ per cent. of copper; it could not be considered as *clean*, for we have seen that the slag produced in melting the cupriferous pig-iron was remelted when it contained only ½ per cent. of copper.

The copper was mechanically mixed in the "loupes cuivreuses," and on an average did not exceed 30 per cent. The sp. gr. of these "loupes" varied from 6·438 to 6·672. One of them was found to have the following composition :—

Iron	76·30
Copper	19·90
Vanadium	0·12
Aluminium	0·43
Calcium, Magnesium	traces
Silicon	0·83
Carbon	0·73
Slag imbedded	3·33
	101·64

This method of treating the cupriferous pig-iron was necessitated by the impossibility of obtaining sufficient copper- or iron-pyrites. The copper is extracted from the "loupes cuivreuses" in the same manner as from the cupriferous pig-iron.

According to Choubine, the cupriferous iron-slag resulting from the treatment of the cupriferous pig-iron in the refining hearth could not, for two reasons, be added to the charge of the ore-furnace: the first is, that on fusion half of the iron is disengaged from a silicate of protoxide of iron of the formula of this slag; and the second is, that the lime and magnesia existing in the copper-ores treated would tend to displace the oxide of iron from the slag, and so favour the formation of ferruginous "bears." In regard to the first reason, I have no knowledge of any experimental evidence in support of Choubine's statement concerning the separation of iron by the simple fusion of a highly basic silicate of prot-

oxide of iron; and the second reason cannot be reconciled with the previous statements that the ore is essentially a cupriferous sandstone, and that not less than 30 per cent. of dolomite was added in order to flux the silica. A portion of this dolomite might surely have been advantageously replaced by slag rich in protoxide of iron.

The black-copper is refined in the Spleissofen of the Germans, which will hereafter be described. It is a kind of reverberatory furnace, having a concave bed of brasque to receive the metal. The surface of the melted copper is exposed to the action of a blast from a twyer, which passes through one side of the furnace. The charge of black-copper was 1965 kil. (about 2 tons). Silicious sand is thrown upon the surface of the melted metal during the whole course of the refining process. The diameter of the nozzle of the blast-pipe was 0^m 04 (1·58 in.), and the pressure of the blast was equal to a column of mercury of 0^m 03 (1·18 in.): the average quantity of air injected per minute was 6·3436 cubic metres (224 cub. ft.). The slag flows out of the furnace through a channel in one side, like litharge in the cupellation of lead. The refined copper is tapped out into circular cavities, from which it may be taken off in discs. These discs are melted in a small refining hearth (Gaarheerd), and when the copper has acquired the proper *pitch*, it is laded into ingot moulds. Choubine gives the following analysis of the refined copper:—

Copper	96·54
Dioxide of copper	1·41
Vanadium	0·21
Iron	0·78
	98·94

The proportion of iron is considerable, and must surely be exceptional. Tin, antimony, and arsenic are stated to be entirely absent from this copper.

Rivot has recently published a description of the smelting of cupriferous sandstone in Perm, from information derived from Le Play;[5] and in the following respects this description differs from that of Choubine. The cupriferous pig-iron is stated to be remelted in a cupola, such as is commonly employed in iron-foundries: the metal is allowed to remain in tranquil fusion during an hour, when it separates into two strata, one of highly ferriferous black-copper, and the other of pig-iron which retains a little copper. The copper is first tapped out, and afterwards the pig-iron, which may be applied to castings where strength is not required. Besides dolomite, from 25 to 30 per cent. of ore-furnace slag is mixed with the ore in the first fusion. The ore-furnace slag which flows from the fore-hearth does not contain more than 0·003 per cent. of copper; and it is stated that this is the *cleanest* slag of all known copper-works. The slag which is tapped out along with the metal contains copper in shots, which is not lost, as the

[5] Principes généraux du traitement des Minérais Métalliques. Paris, 1859, 1. p. 86.

slag is remelted. When the furnace is in good order, the cupriferous pig-iron does not contain more than 3 per cent. of copper.

The theory of the process of copper-smelting in Perm is very simple. The copper exists in the ore in the state of carbonate and silicate, salts in which protoxide of copper is the base. When carbonate of copper is heated to low redness in an atmosphere containing carbonic oxide or in contact with carbon, the copper is easily and completely reduced to the metallic state; and when silicate of copper is exposed to the action of the same reducing agents and lime at a strong red heat, the whole of the copper is also reduced to the metallic state. Now the ore in its descent through the blast furnace is exposed to these conditions of reduction; and not only is the whole of the copper reduced, but a considerable quantity of iron is also reduced and converted into pig-iron. And from the formation of pig-iron it may be inferred, that the iron after reduction must have been during some time in contact with carbon at a much higher temperature than would suffice to effect the reduction of the whole of the copper. The presence of metallic iron would tend to ensure the separation of copper from any silicate of copper which might otherwise escape reduction.

In Rivot's description of the refining of the black-copper, it is stated that "when the fusion is nearly complete, the oxidizing action is diminished, as far as the nature of the fuel (wood) will permit, by ceasing to inject air into the furnace; and a charge of pyritic ores—*i. e.*, sulphides of iron and copper, and silicious fluxes—is then introduced. The matrix of the ore serves to scorify the oxides of iron and copper produced during the fusion; and the excess of sulphur of the pyrites forms with the metals protosulphide of iron and disulphide (protosulfure) of copper."[6] According to Choubine the regulus which is produced in the smelting of certain ores, and which contains 50 per cent. of copper, is not roasted, on account of its small quantity, but is treated in the refining furnace. By the action of sulphide of iron on any silicate of copper in the slag, silicate of protoxide of iron and disulphide of copper would be formed. In about three hours after the addition of the charge of pyritic ore the slag is removed, the blast again let on, and the process concluded in the usual manner. Rivot informs us that "the black-copper subjected to refining contains from 12 to 15 per cent. of carbon and iron."[7] It might be inferred from this language that the black-copper contained a considerable quantity of carbon; and if Rivot intended to convey this impression, he is probably in possession of experimental evidence concerning the combination of carbon and copper, which he has not yet disclosed.

As the copper-ores of Perm are extremely poor, and yet can be smelted with advantage, it will be instructive to inquire concerning the precise conditions under which the smelting is conducted. Accordingly, the following details on this subject from Choubine's description are presented:—

[6] Op. cit., p. 106.

[7] Ibid.

		Pounds (1 Poud = 16 kil. 372 = 36·1 lbs.).	Percentage of copper.	Observations.
Smelted in six blast-furnaces in the course of 40 days	Ores	60000	2·5	The slags are very liquid, and by dry assay yield only inappreciable traces of copper. The method of testing copper-slags by *dry assay* is quite unsatisfactory, and may lead to very erroneous conclusions. A slag may contain a considerable quantity of copper, and yet not yield an appreciable trace of copper by this method. The quantity of air injected into a furnace was 9·64 cub. metres per minute.
	Dolomite	18000	..	
Products obtained	Black-copper	1470	90·0	
	Cupriferous pig-iron	615	15·0	
	Regulus	30	50·0	
	Unclean slags	450	0·3125	
	Total	2565		
Loss of copper on the total copper in the ore and cupriferous products	. . . .	..	4·556	
Ore smelted daily in each furnace	. . . .	250	..	
Charcoal consumed for all the ore smelted, 2350 korobs, or 3·9165 for 100 pouds. 1 korob (korb) of charcoal contains 20 pouds, or 800 pounds Russian.				
Smelting of slag from cupriferous pig-iron (laitier de fer, iron slag) in six blast-furnaces during 36 hours before they were blown-out for reparation	Iron slag	1800	1·5	The cost of smelting 100 pouds of ore amounts to about 3 r. 34¾ cop. arg. (1 rouble = 4 francs = 3*s.* 2*d.* according to average rate of exchange), and 1 cop. arg. (silver copeck = 0,04 franc). Cost of winning 100 pouds of ore and carriage to the smelting-works was 7 r. 22½ cop. arg.
	Unclean ore-furnace slags	1800	0·3	
	Total	3600	..	
Products obtained	Loupes cuivreuses	120	27·0	
Loss of copper	. . . .	..	0·689	
Charcoal consumed, 81 korobs, or 2¼ for 100 pouds.				
Smelting of refinery-slag in a blast-furnace during 42 days	Refinery-slag	9000	5·0	
	Unclean ore-furnace slags	9000	0·3125	
	Total	18000		
Products obtained	Black-copper	450	90·0	
	Cupriferous pig-iron	250	15·0	
	Total	700	..	
Loss of copper	. . . .	..	2·277	
Charcoal consumed, 385 korobs, or 2·139 for 100 pouds.				
Smelting of iron-slag in one blast-furnace during 42 days	Iron-slag	7500	1·5	
	Unclean ore-furnace slag	7500	0·3125	
	Total	15000	..	
Product obtained	Loupes cuivreuses	4500	30·00	
Loss of copper	. . . .	..	0·708	
Charcoal consumed, 300 korobs, or 2 for 100 pouds of mixture.				
Cupriferous pig-iron treated in a refining hearth during 10 days	. . . .	300	15·00	The cost of treating 100 pouds of cupriferous pig-iron was 2 r. 95 cop. arg.
Products obtained	Black-copper	43 lbs 30 (1lb. = 0 kil 4093)	90·00	
	Iron-slag	345	1·50	
	Total	388·30	..	
Loss of copper	. . . .	..	1·00	
Charcoal consumed, 6¾ korobs, or 2¼ for 100 pouds.				
Loupes cuivreuses melted in a refining-hearth during 10 days	. . . .	300	30·00	
Products obtained	Black-copper	95	90·0	
	Iron-slag	260	1·5	
	Total	355	..	
Loss of copper	. . . .	..	0·666	
Refining black-copper in one furnace during 13½ days	. . . .	2625	90·00	According to Choubine, it is more economical to refine the black-copper in the spleissofen with wood as the fuel than in the Gaarheerd with charcoal; in proof of which he adduces the following facts. In refining 100 pouds of black-copper in the spleissofen ⅓ sag. cub. of wood is required; and in remelting 100 pouds of refined copper, which is much more fusible than black-copper, 3½ korobs of charcoal are consumed. But ⅓ sag. of wood yields on an average 1½ korob of charcoal. The charcoal is obtained from the *sapin*, *pin*, and lime-tree.
Products obtained	Refined copper	2360	97·5	
	Refinery-slag	550	5·0	
	Residua	2·20 lbs.	95·0	
	Brasque impregnated with copper	13	3·8	
	Total	2925·20	..	
Loss of copper	. . . .	..	1·30	
Wood consumed, 9¼ cubic sagenes (1 cub. sag. = 2·1336 cub. metres), or ⅓ for 100 pouds.				
Re-melting and casting refined copper in a Gaarheerd during 10 days	. . . .	1250	97·5	Cost of remelting 100 pouds of refined copper was 4 r. 9 cop. arg.
Products obtained	Copper in ingots	1216·10 lbs.	99·5	
	Scrap copper	0·5	99·5	
	Slag	41·10	5·0	
	Total	1257·25	..	
Loss of copper	. . . .	..	0·126	
Charcoal consumed, 43¾ korobs, or 3½ for 100 pouds.				

KERNEL-ROASTING, OR KERNRÖSTEN (German).

This curious and singularly interesting process has already been alluded to (p. 405). When cupriferous iron-pyrites, containing, say from 1 to 2 per cent. of copper, and in lumps about as large as the fist, is subjected to a very gradual roasting with access of air, it is found that a large portion of the copper becomes concentrated in the centre of each lump, forming a nucleus composed essentially of copper, iron, and sulphur. This nucleus is termed the "kernel," whence the appropriate name of "Kernel-roasting." It is enclosed in a more or less porous "shell," or rind, consisting chiefly of sesquioxide of iron, from which it may readily be detached by a few gentle blows with a hammer. The kernels are separated by hand in this manner, and smelted for copper; and the shells are lixiviated with water in order to dissolve out a small quantity of sulphate of copper which they contain. The washed residues, however, still retain copper in the state of oxide, and, probably, also of basic sulphate; they are used to cover the ore during the roasting, and, when the process is conducted in open heaps, to form the bed on which the ore is piled. After having served these purposes they are again lixiviated, in order to extract from them any copper which may have been rendered soluble by the action of sulphuric acid, either directly produced by the decomposition of the sulphate of iron formed in roasting, or generated by the conjoint action of sulphurous acid and atmospheric air (see p. 248, ante).

The process appears to be of comparatively ancient date; but I have not been able to trace its history with certainty. At the present time it appears to be carried on with great skill at Agordo, in the Venetian Alps, where it is stated to have been first introduced in 1692 by a Prussian of the name of Weyberg:[8] it is also practised at Mülbach, in the Tyrol, but not on so great a scale as at Agordo. Swedenborg, in 1734, published an account of the process as then conducted at Agordo, which appears to be precisely similar in principle and results to that now in operation.[9] I am informed by Mr. David Forbes, who was for some years engaged at the Espedal Nickel Works in Norway (now defunct), that kernel-roasting has long been, and still is, practised in Norway.

I shall describe with some detail this process as it is now carried on at Agordo under the direction of Lürzer, to whom I have much pleasure in acknowledging my obligation for a complete and characteristic series of coloured drawings illustrating the successive stages

[8] Mémoire sur les Etablissements d'Agordo (Haute-Vénétie). Par N. Haton, ingénieur des mines. Ann. des Mines, 5. s. 1855. 8. p. 416.

[9] Regnum Subterraneum, sive Minerale de Cupro, 1734, p. 144. The metallurgical works of this remarkable man seem to be very imperfectly known—at least they are rarely if ever quoted; and yet none are, in my judgment, more worthy the attention of those who are interested in the history of metallurgy. They form two tolerably thick folio volumes, copiously illustrated with copperplate engravings, and magnificently printed. I shall have occasion to refer to them especially in connexion with the subject of iron.

through which the ore passes from the commencement of the roasting to the development of the perfect nucleus, and also for drawings of the Styrian kiln, which he has introduced, it is affirmed, with much success.[1] Lürzer promised to furnish me with a detailed description of the process; but, unfortunately, I have not yet received it, and am, therefore, compelled to have recourse to other sources of information. This I much regret, as there are many important points of detail concerning which Lürzer would, doubtless, have given instruction, but which I cannot find in any of the published descriptions of the process. An account of the mode of occurrence, method of working, and metallurgical treatment of the cupriferous ores at Agordo, was published by Haton in 1855;[2] and of this I shall freely avail myself, as I shall also of the short and incomplete notices of the process previously published by Lürzer himself.[3]

Composition of the ore.—It occurs in enormous masses or pockets in a schist of ancient geological date. It is compact, has a brass-yellow colour, and a granular, steel-like fracture; and to the eye it appears free from gangue, though, in reality, it contains quartz finely disseminated through the mass. Its mean composition is stated to be as follows:—

Copper	1·60
Iron	43·15
Sulphur	50·25
Quartz	5·00
	100·00

Lürzer gives the average percentage of copper as 2. The ore, however, varies considerably in respect to the proportion of copper, and may either be entirely free from this metal, or, in exceptional cases, may contain as much as 25 per cent. of it. Lürzer is of opinion that the ore probably consists of an intimate mixture of iron-pyrites (FeS^2), magnetic-pyrites ($Fe^2S^3+5Fe^2S^3$), and copper-pyrites ($Cu^3S+F^2S^3$). Blende occurs finely disseminated in the ore, and occasionally also galena; cobalt is found in the solution of metallic sulphates extracted by washing the roasted shells; tin is present in the copper produced at Agordo, and the ore contains arsenic and antimony, of which the amount may be not less than 2·5 per cent.

The ore is broken in pieces about as large as the fist, and assorted by hand into the five following classes: 1, non-cupriferous pyrites, which is thrown away; 2, poor, containing less than 1·5 per cent. of copper; 3, good, containing from 1·5 to 4 per cent.; 4, best, or rich,

[1] I must not omit also to acknowledge my obligation to Professor Miller, of Cambridge, through whose intervention I received these drawings.

[2] Ann. des Mines, ante cit.

[3] Berg. u. hüttenmännisches Jahrbuch. Tunner, 1853, 3. p. 339; and 1854, 4. p. 242. Rivot has a long article on the subject in his Treatise on the Metallurgy of Copper (1859); and though he seems chiefly to have derived his information from Haton's Memoir, yet on many points he differs from this author. His engravings of the Styrian kiln seem to be copied from those of Haton, but with certain alterations; and if the latter be correct, as they would appear to be from the fact of their agreement with the drawings which I have received from Lürzer, Rivot's engravings are not quite accurate.

generally containing from 4 to 8 per cent. of copper and upwards; 5, containing galena. The proportions raised of poor, good, and rich ores are respectively as the numbers 51·63, 46·16, and 2·22. The rich ores are smelted together with the kernels, &c., in the blast-furnace in the usual way, and are not subjected to the process of kernel-roasting.

Two methods of roasting are practised at Agordo—the old method, in heaps or piles, and the new method, in kilns.

In piles.—They are in the shape of long, truncated, pyramidal heaps, of which the base is rectangular and the transverse section trapezoidal. Their length is variable; they are 6^m (about 19 ft. 8 in.) wide at the base, and 2^m 50 (about 8 ft.) at the top. On an average they contain 209 tonnes (1 tonne = 1000 kil., and is therefore nearly the same as the English ton) of fresh ore. The ground on which the pile rests is excavated to the depth of about 1^m 30 (about 4 ft. 4 in.), and the pit so formed is filled up with the washed ferruginous residues of a previous roasting. Upon the bed thus prepared the pyramidal heap of ore in lumps is raised, care being taken to divide it into sections, in the direction of its length, by four or five inclined beds of ore-dust (schlich), with the view of preventing too free a communication between the different parts of the pile and of intercepting the transverse currents of air. The whole is covered with washed ferruginous residues to the depth of 0^m 12 (about 4¾ in.) or 0^m 15 (6 in.). At the angles of the pile, near the bottom, small cavities are fashioned by means of blocks of wood, and in these small pieces of wood and chips are placed for lighting the pile, which is now done.

In the course of the day the wood is entirely consumed, leaving holes which are stopped up, when combustion continues to be propagated through the mass at the expense of the sulphur in the ore, and the process of roasting proceeds uninterruptedly during eight or ten months. After the lapse of five or six weeks sulphur begins to appear, and is collected. When sulphurous acid has ceased to be evolved, the pile is left to cool for a month, after which the cover is removed and the contents taken to the place where they are broken up.

Sulphur is sublimed from the iron-pyrites, and at first condenses near the surface of the pile; but as the temperature increases it melts, and at this period hemispherical cavities, 0^m 25 (about 10 in.) in diameter, are made in the cover by plunging into it a mould of that shape. These cavities are placed where the disengagement of sulphur appears to be most copious. The sulphur is daily removed from them by means of an iron spoon and poured into a little wooden tub. After some time the cavities become unproductive, when the cover around them must be removed and replaced by fresh matter. The yield of sulphur is only 0·2 per cent. of the ore, or 0·4 per cent. of the total sulphur in the ore.

Styrian kilns.—These kilns were first adopted at Agordo by Lürzer about 1853, and have been found to yield decidedly better results than the old method of roasting in piles or open heaps. The construction of them is represented in the accompanying woodcuts: in fig. 115 a kiln is shown partly in side elevation and partly in section

on the line A, B, C, D, E, F, fig. 116, which is a horizontal section on the line G, H, fig. 115: both these figures are copied from the engravings accompanying Haton's memoir in the Annales des Mines; fig. 117 is a transverse section on the line K, L, fig. 116, and is executed from a drawing supplied by Lürzer to myself. I cannot improve on Haton's description, of which I subjoin nearly a literal translation.

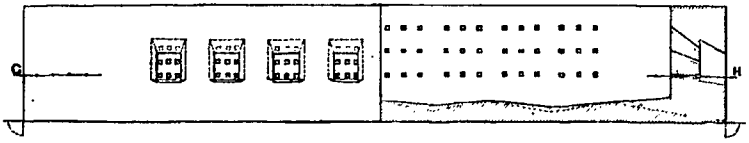

Fig. 115. Side elevation and section on the line A B C D E F, fig. 116.

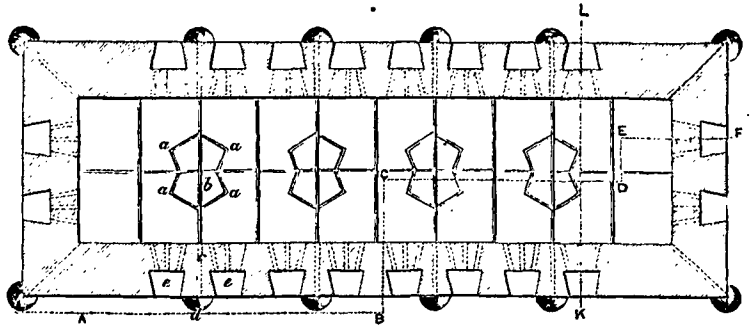

Fig. 116. Horizontal section on the line G H, fig. 115.

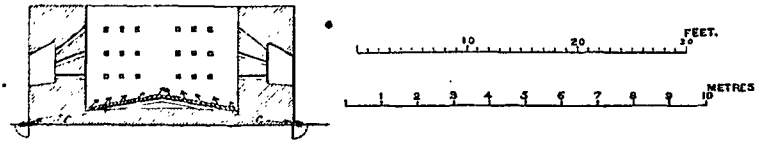

Fig. 117. Vertical section on the line K L, fig. 116.

The kiln consists essentially of a long rectangular enclosure within four walls. It is divided into sections, and the bed of each of these consists of four inclined planes, sloping towards the four angles respectively, thus forming a low pyramid. Along the lines of intersection of these planes with each other are gutters; and other gutters, *a*, *a*, *a*, *a*, are also traced upon the faces of the pyramid, of which *b* is the apex, or the point of junction of the four planes. In the sides of the kiln and on a level with the ground are channels, *c*, *c*, figs. 116, 117, which terminate on the outside in vessels of the shape of a quarter of a sphere: the object of this arrangement is twofold, namely, to regulate the admission of atmospheric air into the interior of the mass, and to allow the sulphur deposited on the bed to flow outwards. There is a channel at each angle for the supply of air required on the ignition of the kiln. In the walls are cavities or chambers, *e*, *e*, intended for the collection of the sulphur; they communicate with the interior by means of nine channels, as shown in fig. 115, which incline and con-

verge somewhat towards the exterior. The length of the kiln is arbitrary. They are protected from rain by roofing of planks.

Mode of charging.—This is begun by placing at the four angles the wood necessary for lighting the kiln, and covering the gutters with flat pebbles of flint. At the top of each pyramid, *b*, chimneys are built up of superimposed courses of ore, which are separated from each other by cubical pieces, so as to form openings into the chimneys. A mixture of ore-dust and water is used in this operation of building. By this arrangement the distribution of air through the whole mass is effected, and kernels are produced from the ore-dust or schlich, which could not be obtained by the old process. The whole of the space between the walls and chimneys is filled with ore, taking care to add alternate layers of *large* and *small* ore, and to place at intervals some beds of chips in order to accelerate the ignition of the kiln. This done, it only remains to rebuild that portion of the wall which it was necessary to pull down in order to remove the former charge of roasted ore, and then to set fire to the wood. When ignition has once been properly effected by means of the wood, combustion is maintained at the expense of the sulphur in the ore, just as in the case of the piles. The roasting is completed in five or six months, and about 288 tonnes of ore are treated at a time. After emptying the kiln the lumps of ore are separated from the ore-dust or schlich and broken with hammers by children, who then detach the kernels from the earthy shells of oxide of iron in which they are enclosed. It is important that none of the kernels should be passed over, as in that case the copper contained in them would not be extracted in the subsequent process of washing the shells to extract the metallic sulphates, and would, consequently, be wholly lost;[4] and it is also desirable that the oxide of iron coating should be separated as completely as practicable. Any imperfectly roasted lumps are put aside to be again roasted.

The average proportions of these various products are stated by Haton to be as under: 13·26 per cent. of kernels and 86·74 of ferruginous shells; of the total weight of kernels 11 per cent. are poor, and 89 per cent. good. The average produces are, for

Good kernels	5·02 per cent.	of copper.
Bad do.	3·45	do.
Ferruginous shells, deduced by calculation ...	0·7041	do.

The consumption of wood required per tonne of raw ore is—

Of cord wood	0st·025 (0·883 cub. ft.)
Of chips	0st·001 (0·03532 cub. ft.)

The roasting requires 7 men, who are employed piece-work, and the

[4] Mr. Petherick assures me that in a recent journey to Spain he visited a locality where a large quantity of cupriferous iron-pyrites is raised, from which the copper is extracted as sulphate after the roasting of the ore; and that all the kernels formed during the roasting *were washed along with the shells, and afterwards thrown away!* Mr. Petherick spoke most confidently to me on this point, and presented me with specimens of the roasted ore which he had himself collected, and which contained distinct and characteristic kernels, small, it must be admitted, yet, one should think, too valuable to be thrown away.

breaking of the ore 121, who ought each to furnish daily 54 kilogrammes (119 lbs.). The quantity of ore treated annually is 15302 tonnes.

Mr. David Forbes informed me (1855) that in Norway, where poor ores of from only ½ to 1 per cent. produce of copper are roasted, kernels are produced which contain generally not more than 7 and never more than 15 per cent. of copper, the former percentage being found the most profitable.

Sulphur is first driven off from the iron-pyrites at the bottom of the kiln, which is the first part to be heated: it runs along the bed into the cavities on the outside prepared for the purpose. As combustion gradually extends upwards through the mass, it escapes successively through the different rows of inclined channels, from which it falls on the bottom of the chambers in the walls of the kiln. Towards the end of the process some cavities are made along the top of the kiln for the collection of sulphur. The crude sulphur thus obtained being necessarily very impure, is refined by fusion in cast-iron vessels. When the sulphur is melted, it is left for some time at rest to allow the foreign matter either to rise to the surface or fall to the bottom. That which rises is skimmed off, and the sulphur is then laded out into wooden moulds formed of two symmetrical parts, which may be clamped together. The charge of sulphur refined at one time is 150 kilogrammes (= about 330 lbs.), and requires from four to five hours. The marketable sulphur obtained amounts to about 1·1 per cent. of the weight of the ore, or 2·2 per cent. of the total sulphur in the ore.

Loss of copper.—It is estimated that in the Agordo process, inclusive of all the operations practised, the loss upon 100 parts of copper amounts to 7·214 or $\frac{1}{14}$th of the whole.

The changes which the ore undergoes in kernel-roasting.—These changes have been carefully investigated by Lürzer, who has described and delineated the appearances presented by the ore during the successive stages of the process, which he divides into four, as follows:—

1*st stage.*—When a lump of ore in this stage is broken across, it is seen to consist of a central mass of unchanged ore, enclosed, as it were, in a rind or shell of a reddish-brown substance like *sesquioxide of iron*; and between the two is interposed a thin more or less continuous layer, which differs in lustre from, and contains more copper than, the original ore, and in appearance resembles *copper-pyrites*. Fig. 118, *a*, *b*, represents the structure of lumps of ore in this stage, which were taken out of the kiln on the 8th and 10th days respectively after lighting. They have been executed from the drawings of Lürzer to which I have previously referred.

2*nd stage.*—This stage occurs at about the middle of the roasting process. The external appearance of the ore is the same as in the 1st stage, but the weight is much diminished. On breaking a lump across, several concentric layers may be observed. In the centre is a nucleus of unchanged ore, surrounded first with a layer similar in appearance to *copper-pyrites*; secondly, with a layer having a greater lustre and of a

reddish colour, similar in appearance to *purple copper-ore* ($3Cu^2S + Fe^2S^3$); thirdly, here and there, with a layer having a metallic lustre and varying from the colour of *indigo copper-ore* (CuS) to that of *vitreous copper* (Cu^2S); lastly, with a thick red-brown crust, forming the outer shell. It will thus be observed that in these concentric layers within the outer shell the proportion of copper successively increased towards the unchanged nucleus of ore; and it has been found that the copper retained in the outer shell is not equably distributed through the mass, but likewise increases towards the interior. When a lump of ore in this stage is broken across, while the interior is still hot, the nucleus on the freshly fractured surface appears surrounded with a radiated ring of a bright red colour, which, however, soon afterwards disappears. In the opinion of Lürzer these rays, without doubt, indicate the course of the gaseous products evolved from the interior.

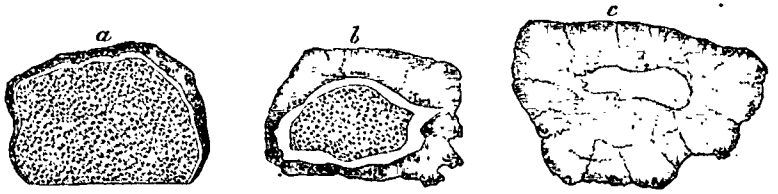

Fig. 118.

3rd stage.—On breaking across a lump of ore in this stage, which occurs when the roasting is nearly completed, a nucleus of unchanged ore can no longer be seen; but within the now greatly increased outer red-brown crust some yellow, reddish, and bluish particles may yet be perceived; and in the crust itself concentric stratification still continues visible.

4th stage.—In this, the final stage, on breaking across a lump of ore it is found to consist only of a central nucleus having the appearance of vitreous copper (Cu^2S), or rather of rich copper regulus, and an outer red-brown shell not usually presenting any indication of concentric arrangement (fig. 118, *c*). Not unfrequently one, two, or more kernels may be formed in a single lump of ore, and the larger the lump the more likely is this to occur.

The following analyses have been made in the laboratory of the Vienna Mint of a kernel, and of the richest or innermost portion of the shell, produced in roasting a *rich* copper-ore :—

Pure kernel.		Innermost portion of the shell.	
Copper	41·64	Copper	3·31
Iron	28·76	Protoxide of copper (CuO)	1·58
Sulphur	29·28	,, iron	0·10
Gangue	0·08	Sesquioxide of iron	85·70
Loss	0·24	Sulphur	0·92
		Sulphuric acid	2·50
		Gangue	2·85
		Loss by heat estimated as water	3·04
	100·00		100·00

This degree of richness in kernels is, of course, quite exceptional, and is due to the fact that they were derived from a copper-ore much

richer than those which in the ordinary course are subjected to the process of kernel-roasting. The average produce of the kernels usually obtained has been previously given. By prolonging the roasting beyond the complete state, metallic copper will be found in the kernel.

It should be borne in mind that the existence of the various compounds of copper described by Lürzer as successively formed in the lump of ore is inferred from external appearances, and not, if I am correct, from the results of analysis.

Theory of the process.—Karsten, Lürzer, Werther,[5] and Plattner have attempted to explain this remarkable process; but their explanations, so far as I can understand them, appear to amount to little more than a detail of certain reactions, which, while they tend to explain the formation of regulus of copper, yet fail to render a rational account of the cause of the actual transference of the metal from every part of a lump of ore and its concentration in a small space in the centre. The phenomenon has been regarded as somewhat, if not strictly, analogous to what takes place in the formation of steel by the cementation process, in which particles of solid carbon are supposed to travel slowly into the interior of a solid bar of wrought iron while heated to strong redness. But this process of cementation is still very obscure, and as much needs explanation as that of kernel-roasting itself.

The results of kernel-roasting clearly establish the fact that when copper-pyrites intermixed with a large excess of iron-pyrites is gradually roasted, the latter may be to a very great extent converted into sesquioxide of iron, while a large portion of the copper remains in combination with sulphur. When iron-pyrites is roasted with access of air at a gradually increasing temperature, sulphate of protoxide of iron is formed, which is subsequently converted into basic sulphate of sesquioxide at the expense of the oxygen of part of the sulphuric acid; and, finally, this basic sulphate, by exposure to a higher temperature, is decomposed, sulphuric acid being evolved in the anhydrous state, which, if the temperature be sufficiently high, may be resolved into sulphurous acid and oxygen. Plattner admits that in roasting iron-pyrites and disulphide of copper analogous reactions occur; and that his contact-action plays a prominent part (see pp. 247, 248, ante).

In kernel-roasting reactions appear to take place in some respects resembling those which occur in copper-smelting, except that silica takes no part, and the iron is separated in the free state as sesquioxide. There is probably the same play of affinities between oxide, sulphate and disulphide of copper, and between oxide of copper and sulphide of iron, &c., as are observed in smelting; and this, I believe, is about all that can in the present state of our knowledge be stated concerning the theory of the process.

I subjoin an extract, nearly literally translated, from Plattner's description of the theory of the process, from which, I think, it will be admitted that he had not the clearest possible notions on the

[5] Berg. u. hüttenm. Zeit. 1853, 12. p. 439.

subject. "The disulphide of copper remaining behind[6]—which comes in contact with the sulphur vapours uninterruptedly escaping in small quantity from the interior towards the surface, where the heat operates, and which, therefore, is not only protected from oxidation, but is also exposed to a higher temperature, produced by the continuous oxidation of the sulphide of iron and of the sulphur vapours with the formation of sulphurous acid and protoxide of iron, as well as of the chief part of the sulphurous acid with the formation of sulphuric acid—passes over in a liquid state, and, in consequence of its affinity for sulphide of iron, combines with the sulphide of iron and sulphide of copper in immediate contact with it, so that an increase is there effected in the proportion of copper."

When silver exists in the ores subjected to the process of kernel-roasting it is stated to become concentrated on the exterior. Mr. David Forbes thus writes to me on the subject (Jan. 15, 1855):—"When silver is present in the ores, it appears to travel outwards, and, in some specimens, I have seen the outer surface of the piece of roasted ore covered by a most beautiful thin shell of metallic silver, as if electro deposited."

WET METHODS OF EXTRACTING COPPER.

Precipitation of Copper from solution by Iron.

The water of copper-mines may contain sulphate of copper in solution. This is the case in the mines of the Isle of Anglesea, where the water is conveyed into shallow pits or tanks containing plates of cast-iron.[7] The copper is precipitated in the metallic state by the iron, and sulphate of protoxide of iron is formed, which, by prolonged exposure to the atmosphere, produces a yellowish-brown mud, consisting of basic sulphate of sesquioxide of iron. The copper is detached at intervals from the surface of the iron, and the solution renewed. The precipitated copper, which is termed cement-copper by the Germans, is melted and refined. The Anglesea or Mona copper has long been highly prized in Birmingham on account of its malleability and ductility.

Bankart's process.[8]

The process was founded on the principle of converting the copper of sulphuretted ores into sulphate by roasting with access of air, and was carried on for some time in the vicinity of Neath and then discontinued. The pyritic ores of Cuba were employed, which contained, on an average, 16 per cent. of copper. The ore was ground under mill-stones. The calciner was constructed in a peculiar

[6] That is, after oxidation of the iron.

[7] Vid. Briefe über die Insel-Anglesea vorzüglich über das dasige Kupfer-Bergwerk u. die dazu gehorigen Schmelzwerke u. Fabriken A. G. L. Lentin. Leipzig, 1800, p. 68; also Aikin's Tour through North Wales, etc., 1797.

[8] A.D. 1845, Aug. 7. No. 10,805. Frederick Bankart, "Improvements in treating certain metallic ores, and refining the products therefrom." I am indebted to Mr. F. Bankart, junr., for the following description.

manner. The floor consisted of tiles, covering long flues, which returned through a double roof. The calciner was charged with 2 tons (= 20 barrows) of ground ore, which was roasted during 24 hours, and stirred at intervals, atmospheric air entering freely through holes at the fire-bridge end and the side-doors, of which, except during the stirring, the lower part only was left open, so that the air might impinge more directly upon the ore. The products of combustion in the fire-place were not allowed to pass over the ore. The calcined ore was drawn out into iron trams, which ran into archways under the bed of the calciner, and which were raised by means of a crane to the washing floors. These floors were filled with wooden *dissolving* vats, 4 ft. 6 in. wide and 3 ft. deep; they were arranged in three tiers, one above another, so that the solution might flow successively from those on the highest to those on the lowest tier. Each vat, at the height of 3 in. above the bottom, had a false bottom, pierced with holes and covered with canvas, tow being stuffed tightly in round the circumference. A wooden spigot was inserted, so that any liquid contained in the space between the two bottoms might be drawn off. Each vat was provided with a steam-pipe and tap. Over each tier of vats was a tramway. Water was supplied to the highest tier of vats by means of a pump and troughs. The canvas on the false bottom having been well wetted, the calcined ore was dropped into the vat from the bottom of the tram, evenly spread, and then covered with as much water as could be safely introduced. Steam was injected into the water through a vulcanised india-rubber pipe, screwed on to the steam-pipe, until complete ebullition occurred. The solution was now drawn off into the next vats below, which had been previously charged with ore, when the heat developed by the action of the anhydrous sulphates in the ore was generally sufficient to cause the hot solution to boil. In like manner this solution was drawn off into the vats on the lowest or third tier. At length a clear saturated solution of sulphate of copper, containing some sulphate of iron, was obtained. The residual ore in the vats was washed with fresh water so long as any sensible amount of sulphate of copper remained undissolved; practically three "waters" were almost always found sufficient for this purpose.

On the ground floor were several rows (about 12) of similar *precipitating* vats, supported on blocks and filled with broken cast-iron or iron plates, each row being 6 inches higher than the next in succession. The solution of sulphates from the lowest tier of the dissolving-vats was allowed to run into the highest precipitating-vats by means of a trough placed under the spigots of the former. A piece of board fixed against the point of influx directed the course of the solution to the bottom of the precipitating-vat. When the vat became filled, the solution, deprived of a greater or less amount of copper, overflowed through a short leaden flap into the vat immediately below, in which also the stream was directed to the bottom. When the solution had thus passed through the series of about 12 vats the whole of the copper was precipitated. It was necessary constantly to brush the broken iron and scrape the plates in order to detach the deposited copper and

expose a fresh surface of iron to the solution. The deposit of copper on the iron plates was so copious and dense that it could be separated in the form of a sheet. Before removing any of the copper in a vat, the whole of the liquor was drawn off into the vat immediately below, and fresh water thrown on the iron and deposited copper in order to wash off any adherent sulphate. The solution left after complete precipitation of the copper contained sulphate of iron: it was evaporated in leaden tanks fixed over flues covered with tiles and then drawn off into vats, in which the salt crystallized.

The lixiviated ore was transferred from the washing vats by copper shovels into wooden trams and conveyed to the roofs of the calciners, where it was spread over the surface and left to dry. When dry it was mixed with $\frac{1}{4}$th part, or 4 barrows, of fresh ore, and the whole was calcined during 12 hours, the oxides of iron and copper in the lixiviated ore greatly facilitating the conversion of the sulphur in the fresh ore into sulphuric acid. The calcined ore was lixiviated as above described, and generally a larger quantity of copper was extracted from the product of the second calcination than from that of the first. The process was repeated three times, and on the last occasion the fresh ore consisted exclusively of iron pyrites. There were thus three calcinations in all. The several tiers of vats were reserved for ore in the successive stages of calcination. The vats on the uppermost tier were kept for fresh ore, those on the second for the product of the second calcination, and so on. In like manner a similar arrangement was adopted in regard to the calciners. The ore from the first tier of vats was conveyed to the top of the second pair of calciners, and so on. The copper was melted and refined in an ordinary refining furnace.

According to Mr. Bankart this method is liable to the following objections:—1. The necessity of grinding the ore; 2. The great bulk of matter which had to be removed several times during the entire process; 3. Especially the loss of copper arising from leakage; 4. The residual ore contained more copper than ordinary ore-furnace slag; 5. The value of the sulphate of iron obtained as an accessary product was far less than the cost of the iron and the crystallization; 6. The refinery slag produced cannot be economised in the same manner as in the process of smelting. The second objection might, in great measure, have been removed by a preliminary fusion and the concentration of the copper in a regulus. The great bulk of the ore would thus have been removed at once, and the expense of grinding the regulus would have been small compared with that of grinding the entire ore. The special advantage of the method is stated to be the production of copper remarkable for purity and malleability; and, at first, sanguine hopes were entertained that it would successfully compete with the process of smelting. Experiments were made under the observation of the late Mr. Richard Phillips with calciners only large enough to receive each about a ton of ore at a time; and it was considered that the experiments were made under very unfavourable conditions compared with such as might be conducted on a larger scale with every appliance suitable. The ore contained 11·62 per cent. of copper, and

was passed through a sieve of 81 holes to the square inch. Mr. Phillips estimated that "the probable expense in coals and wages of extracting a ton of copper precipitate by Mr. Bankart's process, under the proposed improved arrangements, would be from 1*l.* 15*s.* 2*d.* to 15*s.* respectively, according to the per centage of the ore."[9] It is wise never to place too much reliance on the estimated cost of production in comparatively untried metallurgical processes; for metallurgical, like engineering, estimates, have often proved sadly fallacious, and entailed ruin upon too confiding adventurers. The correctness of the preceding estimate of Mr. Phillips, which was, doubtless, most conscientiously given, was not subsequently confirmed. Mr. Bankart has, during many years, abandoned the process, in which he was once a stanch believer, and has ever since been engaged in the ordinary process of smelting. The stern logic of facts is inexorable, and it is the only safe guide in dealing with the schemes of inventors. In Mr. Phillips's report it is stated that the quantity of copper remaining in the residue was not less than 0·62 per cent., a quantity exceeding that which should be allowed to escape in ore-furnace slag.

From what has been previously advanced in this work the theory of Bankart's process should be quite intelligible. There is, however, one point which requires explanation, namely, the use of iron pyrites alone in the last calcination. When this sulphide is roasted under suitable conditions, sulphate of protoxide of iron is produced in the first instance, and is afterwards entirely decomposed, sulphuric acid being evolved and sesquioxide of iron left as a fixed residue. Sulphate of protoxide of iron is decomposed at a lower temperature than sulphate of protoxide of copper. Hence, in the last calcination, iron pyrites is employed in order to furnish sulphuric acid to any oxide of copper which may be present in the calcined ore, and which otherwise might not be extracted.

Wet process by M. Escalle.[1]

This method was practised some years in the vicinity of Marseilles, but the result was not successful, at least in a pecuniary point of view. The ore (containing copper in combination with sulphur), in very fine powder, was calcined in a double-bedded reverberatory furnace. The calcination took place on the bed furthest from the fire. 1000 kil. were thus treated in 12 hours, with a loss in weight of about 17%. The calcination finished, the ore was transferred to the bed nearest the fire, upon which hydrochloric acid at 16° (sp. gr. 1·124) was introduced. The "chloruration" lasted three hours, and the charge consisted of only about one-fourth of that drawn from the

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[9] Printed Copy of Report of Richard Phillips, Esq., F.R.S., F.G.S., etc., on Mr. Frederick Bankart's Patent Process for reducing Copper Ores. Craig's Court, Nov. 26, 1847. This estimate is exclusive of the iron required for precipitation.

[1] Vide Bulletin de la Société de l'Industrie Minérale, T. III. 4ième Livraison, 1858. Notice sur les Usines à Cuivre et les Usines à Antimoine des Bouches-du-Rhône. Par M. L. Simonin, ingénieur civil à Marseille, p. 559.

calcining bed; the whole was rabbled. The chlorides thus produced were dissolved out by water, and the solution was decanted into wooden vessels, polysulphide of calcium, obtained from residues of soda and soapworks by what is called "fermentation," being introduced at the same time. The copper was *first* precipitated, the other metals only being subsequently thrown down. As soon as the liquid ceased to turn blue on the addition of ammonia, the supply of polysulphide was shut off. The supernatant liquor was decanted, and the precipitated sulphide of copper collected. It was drained, dried, compressed, and then moulded into cakes (*pains*). Sulphide of copper (CuS), with excess of sulphur, nearly chemically pure, was thus obtained. These cakes were heated in a sort of blast-furnace in alternation with layers of charcoal. The product obtained was a blackish scoriaceous mass, or *copper-sponge*, mixed with metallic globules; the sulphurous acid generated in this operation was conveyed into leaden chambers to be converted into sulphuric acid. The copper-sponge was remelted, without any addition, in a reverberatory furnace, and yielded in a short time very pure metallic copper.

HÄHNER'S PATENT.

The specification of this patent[2] is in some respects unintelligible to me; but as far as I comprehend it, the process consists essentially in exposing oxide of copper in admixture with chloride of sodium and silica to a red-heat in a reverberatory furnace, by which means chloride or oxychloride of copper and silicate of soda are stated to be produced. Ores in which the copper exists in the state of oxide only require to be pulverized, but sulphuretted ores of copper are first to be roasted *sweet*. If the ore contains no silica, about 10 per cent. of this substance must be added. The chloride of sodium, or other chloride, is intimately mixed with an equal weight of roasted ore, and, if dry, the mixture is moistened. "The moistened chloride, or mixture of chloride and roasted ore, ought then to be incorporated as intimately as possible with the red-hot ore in the furnace, and kept in a continual movement and at a red heat until the smell of muriatic acid becomes less perceptible, and the ore commences to adhere to the workmen's tools," when it is withdrawn from the furnace and a fresh charge added. The roasted product is then lixiviated, if practicable, while still hot, with water acidulated with hydrochloric, sulphuric, or other acid. The copper is thus obtained in solution, and may be precipitated therefrom by any of the ordinary methods.

Mr. Henderson has obtained a patent for the extraction of copper from ores and certain cupriferous products, by heating them in admixture with chloride of sodium, or certain other chlorides, so as to volatilize the copper in combination with chlorine, and condense it in a suitable apparatus.[3] It remains to be seen whether Mr. Henderson

[2] A.D. 1856, No. 571.
[3] A.D. 1859, No. 2900; and A.D. 1860, No. 2525.

will succeed in effectually collecting the gaseous compound of copper: if he should, his condensing apparatus would be a valuable acquisition to the patentee, who proposed that in refining copper a blast of *chlorine* should be projected upon the surface of the melted metal![4]

Remarks on the Patent Laws.

Various patents have been granted for alleged improvements in the treatment of copper-ores, of certain products obtained in the smelting of copper-ores, &c., which are only worthy of notice as affording, as I conceive, satisfactory illustrations of the defective state of our existing Patent Laws.

In one of these patents, the exclusive right is granted of extracting copper by the solvent action of acids from highly silicious ores containing oxides and salts of copper insoluble in water; and also of extracting copper by the same means from sulphuretted ores after they have been subjected to calcination. In another patent Her Majesty confers upon the patentee the monopoly of using sulphuric acid as a solvent for the extraction of copper from ores containing substances insoluble in acids, such as silica![5]

That a man, who has worked out an original and valuable process from his own brain, and who may have incurred great expense in bringing it to a practical issue—it may be after years of protracted toil and anxiety—should have secured to him by law during a moderate term the exclusive privilege of reaping the substantial reward of his own invention appears to me as just and reasonable as that an author should be protected against piratical and unprincipled publishers. But that the law should confer upon a man the exclusive right of appropriating to his own benefit facts which are perfectly familiar to every tyro in chemistry, and of practising operations which are of daily occurrence in the laboratories of chemists, is as impolitic as it is unjust. And, surely, the particular "inventions" above referred to belong to this category. I cordially subscribe to the opinion expressed by Mr. Grove, Q.C., namely, that the real object of patent law was "to reward, not trivial inventions, which stop the way to greater improvements, but substantial boons to the public—not changes such as any experimentalist makes a score a day in his laboratory, but substantial practical discoveries, developed into an available form."[6]

Believing as I do that the existing Patent Laws frequently operate injuriously to the interests of the real inventor, while they afford

[4] A.D. 1849, No. 12,534.

[5] Vid. "Description du traitement du Cuivre par cémentation, pratiqué à l'Usine de Stadtberge, dans la Westphalie; par M. Achille Delesse, Elève-Ingénieur des Mines." Ann. d. Mines, 4 s. 1842, 1. p. 477. The process "consists in passing over the ores acid vapours which decompose the carbonate of copper and convert it into sulphate: the sulphate, after being dissolved out, is treated by iron, which precipitates the copper; the cement-copper is melted in a reverberatory furnace, and afterwards refined in the small hearth." The ores operated on contain copper in the state of carbonate, and are free from any sensible amount of lime.

[6] Suggestions for Improvements in the Administration of the Patent Law.

encouragement to the mere schemer and pilferer of other men's brains, I cannot forbear from directing public attention to the subject through the medium of these pages; and I do so with the less hesitation as there is no manufacturing art which is more likely to suffer from the defective state or administration of these Laws than Metallurgy.

At a recent meeting of the Institution of Mechanical Engineers held at Sheffield, Sir William Armstrong, who presided on the occasion, delivered an address on projectiles, in which he expressed an opinion strongly condemnatory of the present system of Patent Law, and even suggested that an entire abrogation of the law might be beneficial to the community, and not disadvantageous to inventors. Any person who has the pleasure of personally knowing Sir William Armstrong will be convinced that this opinion was as honestly formed as it was candidly stated; and, although I am not prepared to admit that the protection of law should cease to be afforded to really meritorious inventors, yet I entirely concur in many of the observations contained in the following extract from Sir William's address[7]:—

"I am tempted to advert, before I conclude, to a subject intimately connected with mechanical progress, but upon which much difference of opinion may exist. That dauntless spirit which in matters of commerce has led this country to cast off the trammels of protection has resulted in augmented prosperity to the nation, showing the injurious tendencies of class legislation when opposed to general freedom of action. Would that the same bold and enlightened policy were extended, in some degree at least, to matters of invention. Under our present Patent Law we are borne down with an excess of protection. We are obstructed in every direction by patented inventions, which will never be reduced to practice by those who hold them, but which embrace ideas capable of useful application if freed from monopoly. The merit of invention seldom lies in the fundamental conception, but is to be found in the subsequent elaboration, and in the successful struggle with difficulties, unknown to the mere theorist, and often requiring years of labour, blended with disappointment, for their removal. Nothing can be more irrational, therefore, than to give equal privileges to the mere schemer and to the man who gives actual effect to an invention. Primary ideas ought to be the common property of all inventors, and protection, if we are to have it at all, should be sparingly awarded to those persons alone who, by their labour and intellect, give available reality to ideas. Apart from the impolicy of our present indiscriminate system, its operation is unjust. Philosophers who furnish the light of science to guide to useful discovery go altogether unrewarded and unrecognized. Practical men, who, like Watt and George Stephenson, devote the best part of their lives to perfecting inventions of immense importance to the world, seldom derive from patents any greater emolument than would flow to them without the aid of a restrictive system, while they are frequently involved in tormenting litigation about priority of idea. On

[7] From the Report of the Address in the Times, Aug. 2, 1861.

the other hand, we see numerous cases of disproportionate wealth realized by persons whose only merit has been promptitude in seizing upon and monopolising some expedient which lay upon the very surface of things, and required no forcing atmosphere of protection for its discovery. Finally, injustice is done by the existing law to those men who have no desire for monopoly, but who are compelled to become patentees for no other purpose than to prevent their being excluded from carrying their own ideas into practice. For my part, I incline to think that the prestige of successful invention would, as a rule, bring with it sufficient reward, and that protection might be entirely dispensed with. On this point, however, I speak with hesitation; but it is, at all events, certain that extensive reform is urgently required in this branch of legislation, and that the advance of practical science is now grievously obstructed by those very laws which were intended to encourage its progress." [8]

ASSAYING OF COPPER-ORES BY THE CORNISH METHOD.

The successful performance of this process requires great skill and an education of the eye which can only be attained by long and constant practice. In the hands of an expert assayer it is capable of yielding results upon which the smelter may rely with implicit confidence, inasmuch as they are always below the furnace yields; and, considering the nature of the process, it is surprising how closely different assayers will approximate in their *produces*, except with particular descriptions of ore.

Furnace and Implements.

Furnace.—Fig. 119 is a vertical section through the middle of the grate of one of the furnaces used for assaying in the Metallurgical Laboratory. *a* is the fireplace, lined with firebrick, 8 inches square by 12 inches deep; *b* the ash-pit provided with a register door for the regulation of the draught; the door may be entirely opened when the largest supply of air will be obtained, or it may be closed and the register *f* opened in a greater or less degree according to circumstances. This register is formed by a revolving disc of sheet-iron having a semicircular opening, the centre of which coincides with the centre of the door; behind it is another similar semicircular opening in a fixed piece of sheet-iron, *e*, forming the door: the opening of the revolving disc may be made to coincide with the *fixed* opening behind, or it may be adjusted so as to regulate the

[8] Since these observations were in type Sir W. Armstrong has read a paper at the recent meeting of the British Association at Manchester, on the present system of Patent Law, and has strongly contended for its complete abolition. Mr. Fairbairn, the President, in his inaugural address, advocated the expediency and justice of protection, by patents, to really meritorious inventors; but condemned the present indiscriminate system of issuing letters-patent, and animadverted strongly on that class of patentees who are chiefly distinguished by their magpie-like propensity of running away with the silver spoons of real inventors.

admission of air with the greatest nicety. The flue, *d*, communicates with an upright shaft, about 60 feet high, with which five other similar furnaces are connected. When practicable each furnace should have a stack to itself, or, what is equivalent, one stack may be divided into a series of flues, of which there should be one for each furnace. The exterior and the part below the grate are built of common brick. The whole of the brickwork is kept firmly bound together by means of cast-iron plates and wrought-iron tie rods. The furnace mouth can be closed by means of the firebricks, *i*, *h*, each of which is clamped with a piece of flat bar-iron firmly wedged at one end; sometimes a small screw is used instead of wedging: these firebrick covers are of two sizes, and the larger one only need be removed when the crucible is taken out of the furnace. The draught may be regulated not only by the register door of the ash-pit, but also by opening the furnace top in a greater or less degree, or by placing a piece of firebrick in the opening into the flue *c*, or by means of a damper at the top of the stack. With such arrangements perfect control may be obtained over the temperature of the furnace; it can be kept below a dull red or increased sufficiently to melt nickel or manganese. In copper assaying in a furnace of the dimensions stated, 2 or 3 fusions for regulus or 4 calcinations can be made at one time. Furnaces specially constructed for copper assaying are of larger dimensions, so that 4 or more fusions for regulus, or from 6 to 8 calcinations, may be carried on at once; but the size and number of furnaces vary according to the requirements of the assayer. The fuel employed is coke.

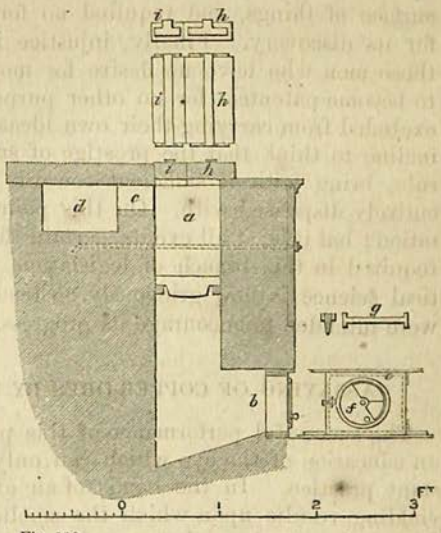

Fig. 119.

Crucibles.—Those known as "*Cornish Crucibles*" are the best: they are sold in nests of two and sometimes three each. The large size (No. 1, fig. 59, p. 222) is used for calcining the ore and fusion for regulus. The smaller and middle sizes are used for calcining the regulus, fusion for coarse copper and refining, according to the quantity operated on. They are sold without covers, a substitute for a cover being made, if required, from a piece of broken crucible. When several assays are carried on simultaneously, the crucible before use should be marked with red chalk, "reddle," or a mixture of hæmatite and water.

Crucible rests or stands.—See fig. 120, A. They consist of a strong iron ring with a slot on each side to receive the ends of the tongs. They are of two sizes, and are used by some assayers for supporting crucibles when out of the furnace.

Crucible tongs.—Fig. 71, p. 231, represents those generally employed by copper assayers: they vary somewhat in size.

Scorifiers or roasting dishes.—They are small, flat, shallow, cup-shaped vessels, made of fireclay, and are employed in roasting or calcining ore or regulus in a muffle. Those used for assaying silver-ores[1] will answer, but if they are made specially for the copper assayer they should be somewhat wider and shallower. The following dimensions are recommended: the cavity about 2½ inches in diameter at the top and ¾ of an inch deep in the centre; ⅛th of an inch in thickness at the top; the height, including the foot, 1¼ inch. In calcining ore one of somewhat larger dimensions is necessary, viz., 3 inches in diameter and ⅞ths of an inch deep.

Flux-spoon or ladle.—It is made of copper, and is used for measuring out the fluxes. Thickness of bowl $\frac{1}{16}$th of an inch, width at the top 1¾ inch, depth ½ inch. The handle is upright, and made of stout copper wire 7 inches in length.

Ladle.—Fig. 120, G. It is made of copper, and is used for drying the sample or for washing the ore to ascertain the nature of the minerals or gangues present.

Regulus bowl or pan.—It may be made of copper, zinc, wood, or earthenware, but the first is to be preferred: it is circular, about 9 or 10 inches diameter at the top and 5 or 6 deep, and is kept partly filled with water for quenching the regulus, slags, &c. About 1 inch below the upper rim is fixed a flat metal ring of sheet-iron, copper, or zinc, about 1½ or 2 inches wide, so as to form a shelf for receiving temporarily the products of fusion. Instead of a shelf, a number of small, finely-perforated, flat copper ladles can be used, made of thin sheet-copper 2½ to 3 inches diameter at the top and ½ inch deep in the centre, with an upright handle of copper wire from 3½ to 4 inches high, and bent in the form of a hook at the top, so that they can be readily suspended from the inside of the bowl and removed when required, the water draining off in the removal; the bottom should be made somewhat flat, that it may stand upright on the table.

Forceps.—Two are required, one of copper, fig. 120, B, and one of steel, fig. 120, C; they are used for manipulating with the slags, regulus, &c.

Copper scoop.—Fig. 120, F. It is used for transferring the fluxes, &c., to the crucible either when out of or in the furnace.

Mould of iron.—Fig. 120, H. It is of the shape generally used by copper assayers; one with somewhat deeper and more hemispherical cavities is preferable: it is employed to receive the slag and regulus poured out after fusion. To prevent the fused products from adhering to it, the cavities from time to time should be rubbed with an oiled rag and

[1] They will be described hereafter.

dusted over with charcoal, or smoked over a gas-flame, or they may be rubbed over with graphite, or a mixture of tar and tallow.

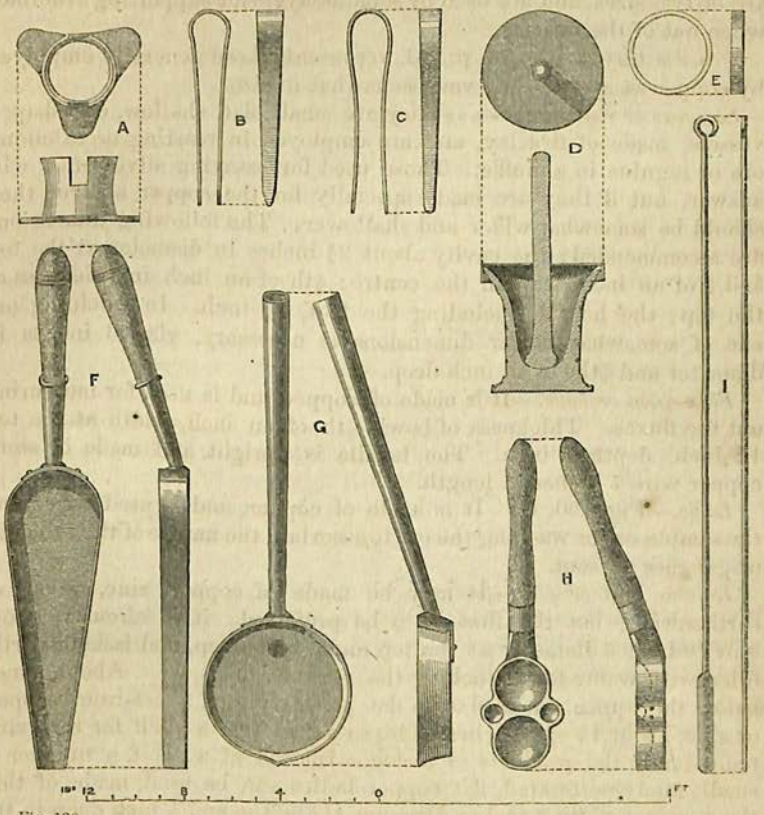

Fig. 120.

Calcining rods.—Fig. 120, I. The blade is usually of wrought-iron, but it is better of steel; it is kept clean by the aid of a rasp or file to prevent adhesion of regulus during roasting: a separate rod is employed for each crucible. When the roasting is conducted in a muffle, a roasting spatula is required; it is made of steel, and is 6 inches in length; it is flattened out at one end into a blade about 2 inches long and from $\frac{3}{8}$ths to $\frac{5}{8}$ths of an inch in width, the other end being fashioned into a point. The blade end is useful for stirring, and the point for breaking up any agglomerated particles during temporary removal from the muffle. A stout iron rod, from $2\frac{1}{2}$ to 3 feet in length, flattened out at one end and bent at right angles at the other, is used for occasional stirring within the muffle.

Steel anvil.—It is used for flattening the copper button upon, &c.; its face should be about 3 inches square.

Hammer.

Chisel.—It is required for cutting the copper buttons, &c.

Iron slab, or flat plate of cast-iron, about 15 inches square and ¾ inch thick, used for breaking down the slags upon, &c. The *iron ring*, fig. 120, E, serves to prevent particles from being lost by projection during manipulation.[2]

Mortar and pestle.—Fig. 120, D, is the mortar made of bronze, and the pestle of iron or steel; a cover is required with a depending rim and having a hole in the centre to admit the handle of the pestle; by this means any particles of the regulus are prevented from being lost by projection out of the mortar during trituration. An iron or steel mortar not quite so deep is to be preferred; a camel-hair pencil or hare's foot is employed in dusting out the mortar.

Sieves.—For sifting samples; they are from 9 to 12 inches in diameter, and are made either of hair or wire, with from 40 to 60 holes to the linear inch.

Slab of cast-iron.—About 22 inches long, 11 wide, and 1 thick, with a border about 1½ inch high, and a *bruiser* with a face about 11 inches wide, 7 long, and 1¾ thick, for grinding down the ore; or a large cast-iron mortar and pestle of the following dimensions may be used as a substitute — internal diameter, near the top, 9 inches, and depth 9 inches. The pestle may be attached by means of a rope to a spring fastened in the wall or ceiling to relieve the arm during trituration.

Balance.—It should carry about 500 grains, and turn with from $\frac{1}{20}$th to $\frac{1}{50}$th of a grain.

Weights.—Special weights, of which the unit is termed *cent*, are used by copper assayers to facilitate calculation. The following table gives the *actual* weights of the *conventional* weights used in the assaying of copper-ores in Cornwall, &c.:—

Assay Weights in cents.		Actual Troy Weight. Grains.		Dwts.		Grains.
100	=	400	=	16	...	16
50	=	200	=	8	...	8
25	=	100	=	4	...	4
20	=	80	=	3	...	8
15	=	60	=	2	...	12
12	=	48	=	2	...	0
10	=	40	=	1	...	16
9	=	36	=	1	...	12
8	=	32	=	1	...	8
7	=	28	=	1	...	4

Assay Weights in cents.		Actual Troy Weight. Grains.		Dwts.		Grains.
6	=	24	=	1	...	
5	=	20	=		...	20
4	=	16	=		...	16
3	=	12	=		...	12
2	=	8	=		...	8
1	=	4	=		...	4
½	=	2	=		...	2
¼	=	1	=		...	1
⅛	=	0·5	=		...	½
$\frac{1}{10}$	=	0·25	=		...	¼

The assays are reported on the 100 parts, the unit being subdivided into ½, ¼, ⅛, and $\frac{1}{10}$ths, and not into decimal parts, so that 28¾ per cent. *produce* is equivalent to 28·75 per cent., &c.

Fluxes, Reagents, &c.

They should be kept in common covered earthenware jars, or in a long rectangular wooden box divided into compartments. The following fluxes are used:—

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[2] An upright block of wood, about 2½ to 3 feet high and 14 inches diameter, having a circular plate of cast-iron about ½ to ¾ inch thick and 14 inches diameter, and an inverted border 2½ inches deep, will be found very useful for many purposes in an assay laboratory.

Borax.—*Dried* or *calcined* borax should be used. Crystallized borax or biborate of soda (NaO, $2BO^3$+10 HO) contains 47·1 per cent. of water; for the purposes of assaying it is desirable to expel this water: when crystallized borax is heated, it melts in its water of crystallization and afterwards swells up to a very light, white, porous, extremely bulky mass, which is *dried* or *calcined* borax. If the temperature is afterwards raised, it fuses into a clear, transparent, colourless liquid, which, after solidification, constitutes *glass of borax*, which is free from water. Much of the so-called dried borax of commerce contains a considerable amount of water, which causes it to swell up or intumesce when heated, an effect which never occurs when it is perfectly dried. Borax has the property of forming fusible compounds with the earthy and metallic oxides, such as lime, oxide of iron, &c., and of rendering silicates more fusible by the formation of borosilicates.

Glass.—Plate or window-glass should be selected, or common green bottle-glass may be used; but flint-glass, which contains oxide of lead in large quantity, should be avoided. With the exception of the latter, all varieties of glass in commerce consist essentially of silica in combination with a fixed alkaline base—chiefly soda—and lime. Green bottle-glass owes its colour to the presence of a sensible amount of oxide of iron. By heating it in a muffle or in a crucible, and plunging it while red hot into cold water, it breaks into small pieces and can then be readily reduced to powder. It is useful in assaying ores containing lime and other earthy bases with little or no silica, and serves to economise borax. Quartz in fine powder may be substituted for it, but glass is to be preferred on account of its fusibility.

Lime.—(CaO). Common powdered *unslaked* lime should be used; but the best is prepared by strongly heating pieces of Carrara marble in a muffle or large crucible until the carbonic acid is expelled; the lime should be slaked when cold, and the hydrate thus formed should be again heated to expel the water; by this means a finely-divided granular variety of dry lime is obtained, which does not absorb carbonic acid with so much rapidity as some varieties of lime. It acts as a flux for silica, silicates of alumina, &c.

Fluor-spar.—Fluoride of calcium (Ca Fl). Care should be taken in selecting it to see that it is free from copper-pyrites, blende, and especially from galena; any lumps containing these minerals should be rejected: it is also desirable that it should be free from quartz, as the presence of this substance would interfere with the easy adjustment of its proportions. The fluor-spar from Derbyshire and the north of England is the best for assay purposes. It melts at high temperatures, and forms very fusible compounds with sulphate of lime (gypsum), sulphate of baryta (heavy spar), phosphate of lime, and silica (see p. 43 ante). It increases the fluidity of the slag, and aids in imparting to it the property of cracking up readily when cold.

Nitre or saltpetre.—Nitrate of potash (KO, NO^5). It is an anhydrous salt, but the crystals contain small quantities of water mechanically

diffused. Common commercial varieties, powdered and dried, should be used. It may be conveniently obtained in a fine state of division by dissolving it in water, and evaporating to dryness, stirring all the while during the latter part of the process. It fuses at a gentle heat without undergoing decomposition. Fused nitre is known as *sal prunella*. Nitrate of soda may also be employed. These nitrates act as powerful oxidising agents by virtue of the large amount of oxygen which they contain, whereby the sulphur of metallic sulphides is converted into sulphurous or sulphuric acids, and the metals into oxides.

Salt.—Chloride of sodium (Na Cl). It decrepitates when heated, and fuses at a red heat into a limpid liquid, and afterwards volatilizes in the form of dense white fumes. On account of its comparatively low specific gravity it generally forms the upper layer in a process of fusion. It should be dried and powdered, and should be free from sulphates which might cause it to retain copper. Some assayers use both dried and undried salt.

Carbonate of soda.—Crystallized carbonate of soda ($NaO, CO^2 + 10HO$). It contains about 63 per cent. of water; when heated it melts in, and afterwards loses, its water of crystallization, becoming a white porous mass. Thus freed from water, it should be used for assay purposes. Bicarbonate of soda, carbonate of potash, or a mixture of carbonate of potash and soda may be used instead of dried carbonate of soda. The alkaline carbonates form very fusible compounds with silica, &c.

Tartar, or Cream of Tartar.—Tartrate of potash, generally known as bitartrate of potash ($KO, HO, \bar{T}$). When pure it is white; but the varieties generally used by assayers are more or less coloured, and sold as *red* or *white argol;* they are cheaper and have a greater reducing power than cream of tartar; they contain foreign carbonaceous matter, tartrate of lime, and other impurities present in the wines from which they are derived.

Sulphur.—It is most convenient to use *flowers of sulphur*, but powdered *roll brimstone* will answer. When pure it is completely volatilized at a gentle heat.

Charcoal.—Finely powdered charcoal is a most useful reducing agent; gunpowder charcoal is best, but anthracite or culm powder, or coke dust may also be used, and for some purposes—as in calcination—are to be preferred, as they burn away less rapidly.

Iron-pyrites.—(FeS^2). Mundic or bisulphide of iron. It should be selected free from copper; many varieties contain small quantities of this metal, but that occurring in the coal measures is generally free from it, on which account it is to be preferred for assay purposes. Sulphide of iron, prepared by adding sulphur to hot scrap or bar iron, or a mixture of hæmatite and sulphur, may be used as a substitute for iron-pyrites.

Refining or white flux.—It is obtained by plunging a red-hot iron rod into the following mixture, when deflagration ensues:—

	By measure.
Nitre	3 parts.
Cream of tartar	2 parts.
Salt	1 part.

The mixture for this purpose should be contained in a large crucible or in a vessel of iron. It should continue to be stirred about until all deflagration ceases. A porous mass is left, which should be reduced to powder; it is generally grey or reddish-grey in colour. The proportions used by different assayers vary somewhat; some omit the salt, others use equal parts of red and white argol in place of cream of tartar. Owing to the varying amount of carbonaceous matter present in the different commercial varieties of argol, the refining-flux may differ considerably in its oxidising power. When a fresh batch of refining-flux is prepared, before use it is better to test its power on a small piece of melted copper: if it is too *sharp*, i. e. too strongly oxidising, argol may be added; or if, on the other hand, it is not sufficiently oxidising, nitre may be added. When nitrate of potash is deflagrated with tartrate of potash, the carbon is oxidised by the oxygen of the nitrate, and carbonate of potash is formed. Refining-flux consists essentially of carbonate of potash, and any undecomposed nitrate of potash, tartrate of potash, and impurities present in these substances—such as lime, &c.—and chloride of sodium. Carbonate of soda or potash mixed with a small percentage of nitre may be used instead of refining-flux. Some assayers prepare two kinds of refining-flux, one containing more nitre than the other; the *strongest*, or that in which there is most nitre, is used for refining very impure coarse-copper buttons.

Sampling.

The method of sampling copper-ores at the mines has already been described. The samples are generally received by the assayer in brown paper parcels of about 1½ lb. weight, occasionally in mass or in small lumps. The ore should be reduced to powder by grinding and rubbing on a flat iron plate, or by trituration in a large mortar, and passed through a sieve of from 40 to 60 holes to the linear inch: the sifted sample should be well mixed. When native copper is present in the ore great care must be taken to ensure a fair average sample, as portions of the metal are often retained on the sieve. The best plan then is to take the total weight of the sample and to assay the sifted portion as well as the portion retained on the sieve. The sample may be dried before or after sifting.

Preliminary Examination.

Before the sample can be assayed, it must be examined as to the character of the ore, the nature of its associated vein-stuff or gangues, the approximate percentage of copper, &c.; and in this examination a practical knowledge of mineralogy is of great advantage. It is necessary to determine beforehand, whether, in the subsequent treatment of the ore, it will require calcination or not, the addition of nitre

or sulphur, &c. The assayer may obtain information for his guidance by resorting to the following expedients:—

a. Washing or vanning a portion of the ore in the copper ladle, fig. 120, G.

b. Testing the ore by means of the mouth blow-pipe, or by chemical tests.

c. Or by making a rough preliminary fusion for regulus, &c., on the ore direct.

The last two methods may prove of service to the uninitiated until they acquire skill by practice. The first expedient is that occasionally adopted by assayers; but a good practical assayer with a quick eye will, by simple inspection of the sample, generally, though not invariably, decide correctly as to the mode of treating it, and it is only in cases of doubt that even vanning is resorted to.

Chief Characteristics of the Process.

The chief peculiarity of the Cornish method of assaying copper-ores is the concentration of the copper in a regulus; and formerly even rich carbonates, oxides, &c., were assayed on this principle. Each assayer has his own peculiarities in manipulation, follows his own rules as to the nature and quantity of fluxes; &c.; but whatever difference there may be in minor details, in the practice of different assayers, the Cornish method always comprises the four following operations:—

1. Fusion for regulus.
2. Roasting of the regulus.
3. Fusion for coarse copper.
4. Refining.

1. *Fusion for regulus.*—The object of the preliminary roasting or the addition of nitre in fusion will be explained hereafter. The result in either case is the expulsion of a portion of the sulphur as sulphurous and sulphuric acids, and the oxidation of a portion of the iron present in excess above that necessary to form a proper regulus, the oxide of iron thus produced being retained in the slag as silicate or boro-silicate of iron, while the remaining copper, iron, and sulphur, together with small quantities of antimony, zinc, &c., fuse into a regulus.

2. *Roasting of the regulus.*—If the regulus be regarded as a compound consisting of disulphide of copper and sulphide of iron, by the process of roasting the whole of the sulphur is eliminated as sulphurous acid, and simultaneously the copper becomes converted into protoxide of copper, and the iron into sesquioxide and magnetic oxide. The clotting which occasionally occurs is due to fusion of the sulphides, or when the regulus is *too fine* to the easy fusibility of the disulphide of copper. If the calcination is conducted at too low a temperature, there is a great tendency to form basic sulphate of copper, which is difficult to decompose at a high temperature, such as may be employed in roasting, without causing the substance of the crucible to be acted upon. When a roasted regulus, containing basic sulphate of copper, is afterwards reduced for coarse copper, disulphide of copper is formed in sensible quantity. If galena or sulphide of lead is present in the

regulus, during roasting it is converted into oxide of lead and sulphate of lead, which, on subsequent fusion for coarse copper, are reduced with the separation of metallic lead, which unites with the copper, and with the formation of sulphide of lead. If sulphide of zinc, tin, or antimony be present in the regulus, by roasting they would be converted into oxides; and in the subsequent fusion a portion of these oxides would be reduced to the metallic state and pass into the copper. A portion of any other metallic oxides which may happen to be present may also be reduced and pass into the copper. Any arsenic which might be present would be partly given off as arsenious acid (AsO^3), and a portion would remain as basic arseniate, which, on subsequent reduction, would be converted into an arsenide, and pass in part into the copper.

3. *Fusion for coarse copper.*—The temperature employed should be sufficient, by the aid of the fluxes used, to reduce the oxide of copper to metal, and the oxide of iron to the state of protoxide, which should be taken up by the borax and be separated as slag. If the button of coarse copper be examined *chemically*, it will be found to contain small quantities both of iron and sulphur, and, it may be, of other metals also. The slag retains a small quantity of copper, but is sometimes practically *clean*.

4. *Refining.*—This operation consists of two distinct stages. In the first the metal is fused and kept so until it becomes clear and bright; sulphur is evolved as sulphurous acid, and the foreign metals present are oxidized by the oxygen of the air and appear as *scum*, but traces of these metals still remain in the copper. In the second stage, on the addition of refining flux, a portion of the copper is oxidized, and dissolves in the metallic copper as dioxide, and copper at *tough-pitch* is produced, or more generally *dry* copper of the copper-smelters. Some oxide of copper is retained in the slag, with the oxides of the foreign metals present; but the greater part of the copper is recovered on subsequently fusing the slag with reducing agents. When copper is melted under salt, it is acted on with the formation of red compound, which has not yet been chemically examined.

Proportions of Fluxes, &c.

Quantity of Ore taken for Assay :—

Copper.	Grs. Troy.	Assay weight marked.
Ores under..... 10%	400 grs.	= 100
Ores from 10 to 30%	200 grs.	= 50
Ores over 30%	100 grs.	= 25

Fusion for regulus.—The fluxes are not usually *weighed*, but only roughly *measured* out by means of the flux spoon or ladle, as weighing would occupy too much time, and would moreover be quite unnecessary in the case of an expert assayer: however, until experience is gained, it is better to note the weights used. In fusion for regulus the proportions of the various fluxes must be so adjusted as to produce a fusible slag with the "gangue" and oxide of iron resulting from the

oxidation of the pyrites, &c., and to ensure that it shall possess the property of easily separating from the regulus; secondly, to ensure the correct proportions of nitre, sulphur, &c., as may be requisite for the formation of a proper regulus.

The following proportions may be taken as an example for the formation of the slag:—

	Grains.		Grains.
Borax	150	to	200
Glass	150	to	200
Lime	200		
Fluor spar	200		

These proportions will produce a very good mixture, fusible in itself and suitable for many ores, and they may be so varied as to produce a slag of the required nature for any ore. It must be borne in mind that borax is more fusible than glass; that these two substances tend to produce a vitreous slag, and act as fluxes for lime, oxide of iron, &c.; that fluor spar increases the fluidity, and aids in imparting to the slag the property of breaking up when cold; that lime also aids in communicating this property to the slag, and acts as a flux for silica, quartz, &c. Some assayers omit glass. It is possible to omit any one of the above-mentioned four ingredients, and yet produce a fusible slag. Borax alone will answer as a flux for many ores, but there is no mixture which more satisfactorily fulfils the required conditions than the one proposed. The quantity used should be from 600 to 800 grs., which is sufficient to ensure the regulus being well covered with slag as it is poured from the crucible.

For the formation of a proper regulus, which should contain about 50 per cent. of copper, we have first to consider if the ore is *yellow* or *grey*.

In *yellow ore*, *i. e.* copper pyrites with or without iron pyrites, &c., more iron and sulphur are present than are necessary to form the desired regulus.

In *grey ore*, *i. e.* vitreous copper, the addition of iron and sulphur is necessary to produce a proper regulus, and these may be conveniently supplied by adding iron pyrites, or a mixture of oxide of iron and sulphur.

TABLE SHOWING THE PROPORTIONS OF IRON AND SULPHUR TO BE OXIDIZED IN ORDER TO OBTAIN FROM YELLOW COPPER-ORE A PROPER REGULUS (WITH ABOUT 50% OF COPPER).

	Formula.	Copper.	Iron.	Sulphur.	Total.
Copper pyrites or "Yellow" Copper-ore	$Cu^2S+Fe^2S^3$	64	56	64	184
Regulus	Cu^2S+FeS	64	28	32	124
To be oxidized	FeS^2		28	32	60

Supposing we had pure copper pyrites to deal with, and wished to produce a regulus containing about 50 per cent. of copper, it will be

seen from the table above that we have to oxidize an amount of iron and sulphur equal to one equivalent of iron-pyrites. This may be done either by partial roasting or "warming," or partly by roasting and partly by the addition of nitre in the subsequent fusion, or simply by fusion with nitre. Either of these three modes may be adopted, and all are resorted to by different assayers, according to the nature of the ore they have to operate on. The first and second methods require considerable experience as to the amount of roasting necessary. The third is the more direct plan: 100 grs. of copper-pyrites will require about 75 grs. of nitre to yield a regulus containing about the correct proportion of copper, and a less amount will be necessary in proportion to the increased amount of earthy matter present.

The following results have been actually obtained by experiment:—

1. 200 grs. of yellow copper-ore from Cornwall, containing 31·42 per cent. of copper and a small amount of quartz, by fusion with 140 grs. of nitre and 200 grs. of each of the fluxes, borax, glass, fluor-spar, and lime, gave a regulus weighing 116 grs., and containing, by calculation, 54·1 per cent. of copper; it was blue on the exterior, was very tender, and had a red-brown semi-metallic fracture. The slag was dark-green, opaque, semi-vitreous, tender, and free from copper.

2. Another specimen of the same ore, fused with the same proportion of nitre and fluxes as in Exp. 1, gave a regulus of similar character weighing 120 grs., and containing, by calculation, 52·36 per cent. of copper. The slag resembled that in the last experiment. The fusion occupied 15 minutes.

100 parts of the ore employed and containing 31·42% of copper require 70% nitre.
Do. *pure* copper-pyrites do. 34·81% do. 77·8% do.

The regulus produced contained rather more than 50 per cent. of copper.

Iron-pyrites (FeS^2), mundic, is often associated or intimately mixed with copper-pyrites, and a portion or the whole of this will very often require to be oxidized. 100 grs. of iron-pyrites, when fused with the above-mentioned fluxes, will require about 180 grs. of nitre to oxidize it, and cause it to pass into the slag.

3. 200 grs. of iron-pyrites from Cornwall, containing 44·68 of iron, and about 2·5 per cent. of silica (quartz), fused with 200 grs. of each of the four fluxes used in Exp. 1 and 400 grains of nitre, gave a black, somewhat glassy, opaque slag free from regulus. The experiment was repeated, and with the same results.

4. 200 grains of the same pyrites, fused with the same proportions of the fluxes used in Exp. 1, and under the same conditions with 335 grs. of nitre, gave a similar slag, and a button of regulus weighing only 2 grs.; it was fibrous, crystalline, and dark iron-grey in colour.

From these experiments we find that the nitre is rather in excess when it amounts to twice the weight of the iron-pyrites, and that 167½ grs. do not quite suffice for 100 grs. of the same kind of pyrites.

The preceding results will guide the assayer in adjusting the pro

portion of nitre, but attention must also be paid to the *mode of conducting the fusion*. The same quantity of nitre, added to an ore, will only yield about the same weight of regulus when the conditions of fusion are the same. Rapidity or slowness of fusion will make a great difference: in the first case the regulus sinks before the nitre has time to complete its action, and in the second case this does not occur. With proper precautions in two experiments with the same ore, the reguluses should only differ a few grains in weight.

TABLE SHOWING THE PROPORTIONS OF IRON AND SULPHUR NECESSARY TO BE ADDED IN ORDER TO OBTAIN A PROPER REGULUS FROM VITREOUS COPPER-ORE.

	Formula.	Copper.	Iron.	Sulphur.	Total.
Vitreous or "grey" copper-ore	Cu^2S	64	..	16	80
To be added	FeS	..	28	16	44
Regulus	$Cu^2S + FeS$	64	28	32	124

Vitreous copper-ore, if fused direct with fluxes, would yield a "too fine" regulus, and copper would be lost in the slag: hence, in order to obtain a proper regulus from this kind of ore, iron and sulphur must be added in the form of iron-pyrites (the excess of sulphur in the pyrites will be driven off in the fusion), or a mixture of oxide of iron and sulphur, or sulphide of iron may be substituted. 100 grs. of disulphide of copper will require about 60 grs. of sulphide of iron (FeS), about 82 of iron-pyrites, or about 55 of hæmatite and excess of sulphur, to yield a regulus containing about 50 per cent. of copper. As many ores contain oxide of iron in the matrix, to such sulphur only need be added.

Purple copper-ore generally contains sufficient copper to yield a proper regulus, containing from 50 to 60 per cent. of copper, by direct fusion with fluxes, and without the addition of nitre or sulphur.

In the adjustment of the nitre to yellow, and of the sulphur to grey, ores, it is customary with some assayers to employ them in nearly the following order:—

1. 3 dwts. of nitre.
2. 3 dwts. of nitre. 1 do. tartar.
3. 3 dwts. of nitre. 2 to 2½ do. tartar.
4. 3 dwts. of nitre. 2 do. tartar. 1 do. sulphur.
5. 3 dwts. of nitre. 2 do. tartar. 2 do. sulphur.
6. 3 dwts. of nitre. 2½ do. tartar. 2½ do. sulphur.

200 grs. (50 grs. of the copper-assay weight) of the ore are fused in the usual way with 3 dwts. of nitre. If the regulus is too coarse, 4, 5, and so on up to 9 dwts. of nitre, should be tried. On the other hand, if 3 dwts. of nitre prove too much, one of the mixtures

2, 3, 4, 5, 6, should be added. It is very seldom these additions have to be resorted to in the order given, as experienced assayers are generally able at once to determine upon the right proportions. It is obvious that in some of these mixtures the ingredients must mutually counteract each other, with respect to the objects for which they are intended. It is also obvious that a true regulus could not be obtained from a grey ore unless iron is present in some form. As a general rule, sulphur is never added to yellow ores.

Fusion for coarse copper.—The reagents generally used for this part of the process are mixtures of tartar and nitre in such proportions that the tartar is always in excess above that required to form carbonate of potash with the nitre. A small quantity of borax is likewise added by some assayers; others use glass instead, others omit both, and others pursue the common practice of adding salt. In the Metallurgical Laboratory we have been accustomed to use carbonate of soda with tartar or charcoal, or, better still, with a mixture of both. The proportions must necessarily vary with the amount of calcined regulus, but the following will serve as a guide:—

	Grains.		Grains.
1.	Carbonate of soda 50 to 150. Tartar .....50 to 150.[3] Borax .....20 to 30.	2.	Tartar .....50 to 200. Nitre .....10 to 50. Borax.....20 to 30.

In the fusion direct for coarse copper, as in assaying carbonates, oxides, silicates, &c., it is better, if the ore does not contain lime, oxide of iron, &c., to add from 20 to 50 grs. of either of these substances, with a view to keep the slag free from copper, more especially when silica is present. The use of too much borax should be avoided, as it tends to retain the copper in the slag.

Fusion of slags from refining or from fusion for coarse copper.—They may be fused with from 50 to 100 grs. of tartar, or less tartar with the addition of from 5 to 10 grs. of charcoal; or the following mixture may be employed:—

Carbonate of soda.....	about 50 grains.
Tartar.....	50 to 100 do.
Charcoal.....	5 to 10 do.

Assay Classification of Ores and Cupriferous Products.

I. Ores, &c., containing over 30 per cent. of copper, which may be fused direct for coarse copper, or, after previous roasting, *without fusion for regulus*:—

a. Native copper, bar copper, &c., require refining only.

b. Black and red oxides, blue and green carbonates, silicates, oxychlorides, require fusion for coarse copper and refining.

c. Various sulphides comparatively pure, or containing arsenic or antimony, rich regulus, &c., require roasting "sweet," fusion for coarse copper, and refining.

[3] Or charcoal 15 to 25 grains.

II. Ores, &c., containing less than about 30 per cent. of copper, which require *a preliminary fusion for regulus* to obtain the copper in a more concentrated form, and to free it from earthy and other impurities:—

a. Ores which require partial calcination, or the addition of nitre, or both, to *remove the excess of sulphur*, and carry a portion of iron and other foreign metals into the slag:—Yellow copper, pyrites, &c., with or without iron-pyrites, blende, galena, &c.

b. Ores which require the *addition of sulphur*, or *of sulphur and iron*, to yield a proper regulus:—

1. Vitreous or "grey" copper-ore.
2. Oxides, poor carbonates, &c.; slags.
3. Poor antimonial and arsenical copper-ores, after having been previously roasted "sweet."

c. Ores which yield a proper regulus by direct fusion:—Purple copper-ore, mixed sulphides and oxides, &c.

To prevent unnecessary repetition, the assay classification will not be followed in the order above stated, but a general description of the method through all stages of the process will be given, leaving it to the judgment of the operator to apply the particular part applicable to the kind of ore submitted to assay.

Practical Directions for Conducting the Process.

1. *Fusion for regulus.*—The ore, "raw" or calcined, is intimately mixed with the fluxes, borax, glass, lime, fluor-spar, nitre, iron-pyrites, or a substitute for the latter, in accordance with the directions already given. The mixture is generally made in No. 1 crucible by means of a small steel spatula, and may be covered with a thin layer of borax or of the mixed fluxes. When a preliminary calcination is resorted to, the crucible in which this operation is performed should be reserved for the subsequent fusion; or should a scorifier be employed, it should be reserved for the subsequent calcination of the regulus. In calcination the ore should be exposed to a dull red heat until the blue flame of sulphur ceases, and the surface appears reddish-brown, which usually occurs in about ten minutes. The crucible or scorifier is then taken out and allowed to cool. If much iron-pyrites, blende, &c., is present, the calcination must be prolonged. The crucibles, when placed in the furnace, should be packed well round with coke, up to, but not above, them, so that they may be as uniformly heated as possible. Covers are generally dispensed with; but, if used, they should be placed slightly on one side, so as to leave space for the free escape of the gases evolved, otherwise the fused matter is liable to run over the sides of the crucible. A cover may be useful in preventing particles of fuel from being projected into the crucible. The crucibles being arranged, and the furnace-top closed or left slightly open at the back, the temperature is gradually raised, so that the fusion may be completed in from fifteen to twenty minutes. During the first part of the

fusion, effervescence occurs from the escape of carbonic, sulphurous, and nitrous acids, and the vapour of water; but it gradually diminishes, until, at the close of the fusion, the surface of the slag is perfectly tranquil. The crucible is now quickly removed from the furnace, and made to receive a rotary motion in order to wash down any particles adhering to the sides, immediately after which the melted contents are poured into an iron mould (fig. 120, II). The interior of the crucible must be examined *while hot*, to ascertain that no globules of regulus remain attached to the internal surface. As soon as the slag has solidified, or is "set," it is seized with the forceps (fig. 120, B); plunged two or three times into cold water, and then left to cool. This immersion in water cracks up the slag, and causes the regulus to be more easily detached when cold. The use of the hammer should be avoided, as the regulus is very fragile; and it is moreover unnecessary, if proper precautions have been observed. If any slag adheres to the regulus, it is generally on the upper surface, from which it may be detached by gentle taps with a small hammer, or by means of a spatula-blade. After the regulus is separated, the slag should be examined to see that there are no globules of regulus remaining in it; and should any be present, they will generally be found at or near the external surface. The presence of regulus in the slag most frequently arises from the latter not having been sufficiently fluid, or it may be caused by the projection of particles of fuel into the crucible during fusion. When all the conditions are right, the slag will be free from all traces of copper-regulus.

To save time and trouble the slag may be poured into one cavity of the mould and the regulus into another; but considerable practice is required to enable the operator to do this successfully. If the regulus is not easily detached, or if there is any doubt respecting the *cleanness* of the slag, the latter may be broken in pieces and re-melted with a little sulphur or iron-pyrites, when the small button of regulus which may be thus formed must be added to the regulus previously obtained.

The *slag* is generally opaque, or more or less glassy, and varies in colour from white, grey, pale-green, bottle-green, to black; the lighter-coloured slags are generally produced from "*grey*" ores, and the darker-coloured ones from "*yellow*" ores, &c., the dark colour being due to oxide of iron. Occasionally the oxide of iron imparts a bluish colour to the slag; but it differs in tint from that sometimes produced by protoxide of copper. The colour of the slag should be uniform throughout, and not variegated, mottled, or streaked, as this generally arises from imperfect fusion. It should be free from every trace of red colour, which would indicate the presence of copper as dioxide. A proper slag breaks up easily, or crumbles into small angular fragments under slight pressure. This property of the slag is very advantageous in causing the easy separation of the fragile regulus, and is due to the use of fluor-spar or lime. If the slag is too glassy, it has a tendency to adhere to the regulus, an evil which may be counteracted on a subsequent fusion by increasing the amount of lime or fluor-spar, or both, as the case may require. If the slag flows thick from

the crucible and has a stony aspect when cold, or the crucible is much corroded or cut into at the line of junction with the upper surface of the slag during fusion, there will generally be found to have been excess of lime and sometimes excess of fluor-spar. It is a common practice to use a layer of salt as a cover for the mixture during fusion: salt acts as a lubricator to the sides of the crucible, and allows the gases produced in the reactions to escape more freely from the surface of the slag during fusion. There are, however, some objections to its use. The fumes which it produces and its extreme fusibility prevent the assayer from observing whether the slag underneath has the proper degree of liquidity. When salt is used, on pouring out the fused contents of the crucible, it will be found on the top of the slag, and should be crystalline and white or greyish-white in colour; but if it has a pink or red colour, it is a sign that copper is present in sensible quantity.

A *good* or proper regulus should be reddish-brown in colour, more or less convex on the upper surface, very tender, full of cracks or fissures, easily broken up into fragments and reduced to powder. The reddish-brown colour is due to the surface being studded with fine particles of metallic copper, or *moss-copper* in miniature. It is also obtained of a blue colour, when it corresponds to the "*blue-metal*" of the copper-smelters. It should contain about 50% of copper; but the produce may vary from 40 to 60%. It is not desirable to obtain it richer in copper. A good regulus is more easily calcined than one *too coarse* or *too fine*.

A *coarse* regulus is dull and coarse-grained on the exterior, more or less flat, and sometimes vesicular on the upper surface, is comparatively hard, and varies in colour from iron-grey to brass-yellow, according to the amount of iron and copper present; but it readily acquires a red, purple, or blue tarnish; its proper colour can best be seen by inspecting a *clean, fresh* fracture when *quite cold;* the fracture is crystalline, fibrous, or coarsely granular. It is not so easily reduced to powder as a proper regulus, and the powder is lighter in colour; it corresponds to the *coarse-metal* of the copper-smelters. There is little fear of the slags retaining copper when a *coarse* regulus is produced; but the calcination is not quite so readily effected without the formation of sulphates, and the time of calcination is prolonged in a degree proportionate to the amount of iron and sulphur present above what may be necessary to form the proper regulus. It may be desirable occasionally, when operating on a very poor ore or slags to obtain a coarse regulus, to increase the bulk, and so facilitate the collection of the copper.

If the regulus is too *fine*, it is more or less round, and the external surface is very smooth and bright, semi-metallic in lustre, and nearly black in colour; its fracture is glassy or very compact in structure, and dark bluish-grey in colour; it is comparatively hard when broken; the powder is nearly black, and has a bluish tinge; it is more difficult to calcine than the proper regulus, owing to its greater tendency to fuse. Moreover, when the regulus is too *fine*, copper is liable to be retained in the accompanying slag; and although it is *possible* to pro-

duce a comparatively fine regulus with a slag free from copper, yet it is not safe or desirable to do so and run the risk of losing copper.

Occasionally the regulus will rapidly crumble into fine powder, which may arise from imperfect fusion, from its containing excess of sulphide of iron, or from leaving it too long in contact with water. The presence of other metals, such as lead, zinc, antimony, arsenic, &c., alters the character of the regulus.

The following are some analyses of the three kinds of regulus, *good*, *coarse*, and *fine*, obtained from an experienced Cornish copper assayer, and analysed by Mr. R. Daintree, while a student in the Metallurgical Laboratory[4]:—

	"Coarse."		"Good."		"Fine."	
	By analysis.	By theory.	By analysis.	By theory.	By analysis.	By theory.
Copper	27·74	26·90	58·61	58·26	72·70	73·04
Iron	35·05	35·70	16·50	17·15	5·42	5·38
Sulphur	37·10	37·40	24·76	24·46	21·80	21·51
	99·89	100·0	99·87	100·00	99·92	100·00
Formula	$2Cu^2S + 3Fe^2S^3$		$3Cu^2S + 2FeS$		$6Cu^2S + FeS$	
or	$Cu^2S + 1\frac{1}{2}Fe^2S^3$		$Cu^2S + \frac{2}{3}FeS$		$Cu^2S + \frac{1}{6}FeS$	

Each of the preceding results is the mean of three determinations of each ingredient. The copper was determined by standard solution of cyanide of potassium: the iron by standard solution of bichromate of potash; and the sulphur as sulphate of baryta. On comparing these analyses with those of the products of copper-smelting, they will be found to correspond in composition to *coarse*, *blue*, and *white* metal respectively.

2. *Calcination of the regulus.*—It is first reduced to fine powder in an iron or bronze mortar, fig. 120, D, and, after the removal of the powdered regulus, a little coke-dust or anthracite powder is rubbed down in the mortar and afterwards added to the regulus. Thus finely divided, it is introduced into a No. 2 crucible or scorifier.

If a *scorifier* is used, its internal surface should be previously rubbed over with the unctuous variety of hæmatite powder, whereby the removal of the calcined regulus is facilitated and loss by adhesion prevented. The scorifier, containing the regulus evenly spread, is placed in a muffle, which may be filled with as many as it will conveniently hold. The calcination is conducted at a gradually-increasing temperature, the muffle door being left open all the while. The regulus should be stirred occasionally during the process with a *roasting spatula* on temporary removal from the muffle, or by means of the *stirring-rod* within the muffle. Calcination takes place more readily in a muffle, and does not require so much attention as when it is effected in a

[4] Mr. Daintree was an excellent manipulator. He is now in Australia, where he has long resided.

crucible in the furnace, very little stirring being necessary. If it is not pulverulent on completion of the process and shows any sign of clotting, or if there is any other reason for supposing that it has not been perfectly calcined, it must be rubbed down with about 20 grains of anthracite powder, and re-calcined for about 10 minutes. When the calcination is ended, the scorifier is taken out of the muffle; and, when cool, the contents are transferred to crucibles ready for fusion. The scorifiers may be used over again for the same purpose.

The common practice is to effect the calcination in a *crucible*, selecting the smaller or middle size according to the quantity of regulus. Several calcinations may be carried on in one furnace at the same time. The furnace is filled with fresh fuel to within a short distance of the top, and the crucibles are then introduced and placed firmly with a slight inclination forwards, so that a current of air may pass over the surface of the regulus powder. A stirring-rod, fig. 120, I, is put into each crucible, with the broad end downwards, the upper end being held between the fingers of the left hand, or allowed to lean against some support to facilitate the manipulation. The calcination should commence at a dull red-heat, which should be gradually, but as quickly as is compatible with a proper calcination, increased to a strong red-heat. Constant stirring is necessary for the first 15 or 20 minutes, but afterwards it need only be occasional. The time required for complete calcination is about 30 minutes, and sometimes three-quarters of an hour. If the temperature is too low at first, there is a tendency to form basic sulphate of copper, which gives a greyish tinge to the surface of the powder and prolongs the calcination. Too high a temperature occasions clotting, and so prevents oxidation. When clotting occurs, the regulus must be removed and triturated with a little coke-dust or anthracite, and afterwards put back into the crucible, and the calcination proceeded with; but in such cases it is best to throw it away and begin afresh. At the right temperature the powder will remain in a sandy state and be very easily kept glowing at first. If the powder shows the least sign of softening or of clotting, the temperature should be lowered immediately by raising the crucible for a few seconds and placing under it some pieces of fresh coke. The calcination is completed when it is "sweet," *i. e.* when the odour of sulphurous acid can no longer be detected. The crucible and rod are now removed from the furnace and allowed to cool. When cold the roasted regulus has a greyish-black colour. If any portion adheres to the rod, it is filed or scraped off and returned to the crucible. The same crucibles are used for the subsequent fusion.

3. *Fusion for coarse copper.*—The calcined regulus is mixed in the crucible with the proper fluxes, and then put into the furnace, the fire being "hot." Fusion occurs in about 10 or 15 minutes. The fusion should be rapidly effected, and as soon as effervescence ceases the melted contents are poured into a mould; when the slag is set, the button is dipped into cold water, or the whole is allowed to cool. The *slag* should be black, glassy, and tender; if it contains copper it presents streaks or patches of a red colour; this is best observed by

examining the exterior of the slag or the interior glaze of the crucible used in the fusion. This red colour may be due to deficiency of reducing agent, the presence of too much borax, or to too low or too high a temperature during fusion; or to keeping the copper too long in a state of fusion, when the metal has a tendency to become oxidized and pass into the slag. The interior of the crucible and the slag should be examined to see that no prills or small globules of metal are present: none will be found after a successful fusion. The slags are retained for subsequent fusion, which, though commonly practised, is often unnecessary.

The *button* of coarse copper should be easily detached from the slag and have a clean surface; if it is black or covered with regulus, the previous calcination has been imperfect, the coating of regulus being due to sulphide left unoxidized or to sulphates formed in the roasting having been again reduced to sulphides. When this evil occurs, the whole should be rejected and the assay begun again. The coarse copper is generally convex on the upper surface and somewhat rough towards the centre; after nicking it with a chisel it breaks short in the vice when struck, and the fracture is fine-grained, dull, and greyish or orange in tint; occasionally, when produced from pure ores, it has the properties of fine copper. Its character necessarily varies according to the impurities present. Peculiarities which have been observed in connexion with the presence of various metals are as follow:—

Iron.—It is often present in small quantities under 1 per cent., and is not objectionable, as it tends to render the accompanying slag free from copper, and it passes out easily on refining. When it is present in larger quantity the copper is harder and paler in colour, and the convexity of the upper surface of the button is increased: the latter is not easily fractured, and is more difficult to fuse than copper, and occasionally subsides as an irregularly-shaped, imperfectly-fused mass. The conditions which favour the passage of iron into the copper are excess of reducing agent and a high temperature.

The results of the following experiment will illustrate the mode of formation of this ferriferous copper. An intimate mixture consisting of

	Grains.
Protoxide of copper (CuO).....	200
Hæmatite	100
Charcoal	100
Carbonate of soda.....	300
Borax	30

was exposed in a covered Cornish crucible to a high temperature for more than half an hour. A black, glassy slag was produced, presenting on its external surface small patches of a red colour; and a well-melted, clean, bright, metallic button was formed of a pale copper-colour, and weighing 210 grains: it was composed of

Copper	71·08
Iron	28·23
	99·31

Tin.—It hardens the copper and renders the exterior browner in

colour; even when present to the extent only of 5 per cent., the fracture of the copper is not much altered, though it is somewhat paler in colour; it is difficult to recognise the presence of tin in small quantity from the physical characters of the copper, except that of increased hardness.

Lead.—When lead is present even in considerable quantity the button on the exterior will retain its copper colour and be soft and malleable; but it has a characteristic dull, bluish-grey, granular fracture; the button is often accompanied by a regulus when lead is present, the sulphate of lead which is formed in the process of calcination becoming reduced during the fusion. Lead is the *great curse* of the copper assayer.

Antimony.—It renders the copper hard and brittle, and communicates to the fracture a dull yellowish-grey colour; when it exceeds 10 per cent. the fracture has an iron-grey colour, and the copper is very brittle.

Zinc.—It is not easily recognized in small quantity, as in this case its presence does not much alter the character of the copper; it tends to communicate a yellow colour and fibrous crystalline fracture to the copper.

Arsenic.—It renders the copper harder, brittle, and greyer in colour.

Nickel.—It is occasionally present, when it renders the copper harder and paler in colour.

Silver.—It often occurs in copper from true grey copper-ores; but when present in small quantity it cannot be detected by the physical characters of the copper.

Gold.—It is rarely present in appreciable quantity; but occasionally it is found accompanying silver.

4. *Refining.*—The crucible which has been used for the fusion of coarse copper is usually employed for refining. The process is conducted as follows:—The crucible is placed well down in the fire, with the centre directly under the line of junction of the two bricks used to close the furnace; and, when it has become bright red-hot, the button of coarse copper is dropped quickly into it, the furnace is closed and watched attentively through the crevices between the bricks above mentioned. Fusion soon occurs, and at first slight evolution of gas takes place from the dull surface of the metal; after a short time the coating of oxides rapidly clears off and the surface becomes bright and resplendent round the edges; and from the centre bright and bluish-green light is reflected, producing the appearance technically termed the "eye" or "star." Some refining flux or refining flux and salt, previously placed ready in the copper scoop, fig. 120, F, is now quickly projected on the top of the fused button, and the furnace is closed; after the lapse of about 2 minutes the crucible is removed and its contents poured out into the mould. The button should come out covered with slag; and when set it is seized with the forceps and its under surface made to touch the water in the bowl, by which means the slag is readily detached. The whole process of refining should occupy from 5 to 10 minutes.

The *slag* is grey, flesh-coloured, pink, or pale-red, and separates

easily from the button; occasionally it is blue, bluish-green, or green, from the presence of protoxide of copper; or it may be deep-red from the presence of dioxide of copper; and this arises from the copper having been too much oxidized before the refining mixture was projected on it, or from the flux itself being too *sharp*, *i.e.* too strongly oxidizing.

The *button*, when "fine," is more or less flat, and its upper surface is coated with a thin orange-red film; the copper is soft, malleable, tough, and breaks with difficulty, and its fracture is finely silky. More commonly it is *dryer* and has an indentation or *pit* on the upper surface, and when broken across the fracture is granular and has a purplish-red colour. If not sufficiently refined, the copper has more the appearance of coarse copper externally and when fractured: in this case the refining process should be repeated. When over-refined, the copper is coated with a thick, red, rose, or crimson-red film, and it is then said to be *burnt*; the slag is red, and adheres to the button, which is brittle, and when broken across presents a deep-red somewhat porous fracture.

Salt is generally used in refining: it serves to dilute and check the too rapid action of the refining flux, and may also aid in the separation of the antimony, lead, &c.; but the refining flux may be used alone. When the flux is too "sharp," or not "sharp" enough, it may be modified by adding a small quantity of tartar or nitre respectively, before projecting it into the crucible. When the coarse copper is very impure, from the presence of iron, tin, lead, antimony, zinc, &c., a small quantity of borax may be added with advantage when the button is first put into the crucible; it dissolves the scum, and the button "cleans" more readily. Occasionally it may be necessary to lift the crucible up, and resort to gentle shaking or tapping to break the crust on the surface of the button. Some assayers subject the coarse copper button, before refining it, to one or more meltings with a refining flux; the process is called "washing."

Lead is difficult to remove in refining without some copper passing into the slag.

Antimony is also difficult of separation, and a *small* quantity of lead is generally added to aid in its removal; but it may be separated without lead by the use of a refining flux a little more oxidizing.

Tin retards the appearance of the "eye" in refining.

Silver, which rarely exceeds in amount 1 per cent. of the ore, remains in the copper after refining. The whole, or nearly so, of the silver originally present in the ore becomes thus concentrated in the copper. If present in sufficient quantity materially to affect the per-centage of copper, the button should be assayed for silver by cupellation, and the weight of the silver found deducted from the total weight of the original button of copper.

Cleaning of slags obtained in refining.—The slag from the refining process always contains copper. It should be roughly powdered, mixed with some tartar, charcoal, &c., fused, and poured out into the mould. When cold, the product is broken down and carefully examined for small *prills* or shots of copper. The prills obtained generally weigh

from 1 to 5 grs., according to the quantity and purity of the button subjected to refining, and the skill of the operator; they are added to the button of fine copper and weighed; they are always refined by copper assayers, but their weight is often so small that the loss which they undergo in the process is *practically* unimportant. The fusion requires from 10 to 15 minutes; the slag should be black. If it is considered necessary to clean the slag from the coarse copper fusion, it may be intermixed with the refining slag, and one fusion will suffice for both.

The loss of copper in the Cornish method of assay.—If any loss occurs in the preliminary roasting or subsequent fusion for regulus, it is from fine particles being carried off in calcination, or from small entangled shots of regulus being retained in the slag. The chief loss of copper occurs in the fusion for coarse copper and in the subsequent refining; for if the slags be tested chemically, they will be found to contain small quantities of copper, the proportion varying according to the richness of the ore, and the amount and nature of the foreign metals present, especially lead. The discrepancies between the results of different assayers arise chiefly from the manner in which the process of refining is carried on. It is the most difficult part of the process, requiring much skill and judgment for its accurate performance; and through inattention or want of experience, a large amount of copper may be lost in this final operation. The actual loss of copper decreases in proportion to the richness of the ore; but the difference between two assays—one by the *dry* and the other by the *wet* method—increases in proportion to the richness of the ore. This statement must be taken in a very general sense, as the presence of other metals, the nature of the ore, &c., will modify the result of the dry assay considerably.[5]

Special Modes of Assaying particular kinds of Ores and other Cupriferous Products.

Native copper.—Simple fusion with a small quantity of tartar, or charcoal and carbonate of soda, is often sufficient to yield a button of *fine* copper; if not, the button must be subjected to the process of refining. The slags in either case should be *cleaned* as usual by remelting with a reducing flux. If it is intermixed with oxide, carbonate, &c., the proportions of reducing agents should be increased.

Bar copper generally requires melting and refining. It is well to glaze the interior of the crucible before use, which is readily done by melting in it a little borax.

Oxychloride of copper.—This should be fused direct with carbonate of

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[5] *The German method of assaying copper-ores.*—I shall not enter upon a description of this method in the present volume. The copper, if not present in the state of oxide in the ore, is converted into oxide by *roasting sweet*. The roasted product is melted with borax and black-flux, whereby the copper is reduced in a state of greater or less purity. The reduced copper is refined by scorification with lead in a muffle; and certain allowances are made to compensate for the loss of copper in the slag. This process of assaying is sensibly inaccurate.

soda and a reducing agent, such as charcoal, tartar, &c. No object would be gained by roasting. The coarse copper is refined if necessary.

Regulus.—Rich regulus. 1. It should be reduced to powder, and calcined in a scorifier or crucible, with the usual precautions. To complete the calcination, it should be afterwards rubbed down with 20 or 30 grs. of coke-dust or anthracite-powder, and re-calcined. If not thus treated, it is liable to retain sulphates which would occasion loss, and yield a regulus, on fusion for coarse copper. 2. Fused for coarse copper. 3. Refined. As "British regulus" is generally poor in copper, a portion of the iron and sulphur should be first removed by partial calcination, or, as it is technically termed, "warming," or by the addition of nitre; after which it must be fused for regulus, and the process continued in the usual manner.

Slags.—They are generally silicates of protoxide of iron, &c., containing copper. The best method of cleaning them is to fuse direct, with the addition of iron-pyrites, and so collect the copper in a somewhat coarse regulus.

Foreign Metals occurring in Copper-Ores, &c.

Tin.—It occurs in copper-ores chiefly as oxide of tin (tin-stone), or as sulphide of tin and copper (bell-metal ore). When present as oxide, the greater part will be carried into the slag by fusion with nitre, &c.; but when it exists as sulphide, or when other sulphides are present in large proportion, the ore should be subjected to a preliminary calcination before fusion for regulus, so as to obtain a richer regulus than would otherwise be produced, as in this case the tin tends to pass into the slag as oxide.

Iron.—It occurs in the state of iron-pyrites or mundic, arsenical iron-pyrites, mispickel, oxide, &c. By calcination or the use of nitre there is no difficulty in causing any quantity of iron to pass into the slag in the state of oxide.

Zinc.—It is generally present as sulphide in the form of blende or *black jack*. Calcination or the use of nitre are the only means resorted to to oxidize the zinc and carry it into the slag, care being taken to ensure the presence of sufficient iron and sulphur to form the proper regulus.

Lead.—It is generally present as sulphide of lead or galena, but occurs in true grey copper-ores. Its presence occasions much trouble to the copper-assayer, because, even by prolonged calcination, it cannot be made to pass into the slag, and will be found in the regulus and coarse copper. The following is the best mode of treating an ore containing lead:—If iron-pyrites is present, the preliminary roasting or addition of nitre may be omitted, and the ore fused at once for regulus; and when the latter is in the state of fusion a few grains of iron-wire should be dropped into it, or the end of a thin rod of iron may be kept immersed in it for about ten minutes. The rod should then be withdrawn, and the regulus poured out and left to cool. On detaching the regulus (which should be coarse) when cold, the lead

will be found as a button at the bottom, and, if in small quantity, diffused as globules. It can be separated from the regulus by bruising in a mortar, when the flattened particles of the metal may be picked out. The regulus may afterwards be treated as a yellow copper-ore in the usual way. The lead will contain some copper, which can be best estimated by the wet way. If the ore does not contain iron-pyrites, it should be added, as in the case of grey ores, &c. There will be some difficulty in applying this method at first, in ensuring the right conditions suitable for each ore; but it is the most effectual with which we are acquainted, and, if properly conducted, no further trouble will be experienced from the presence of lead in roasting the regulus, fusion for coarse copper, &c.

Antimony.—It is generally present in some varieties of fahlerz, or *true grey copper-ore.* In the case of rich ores, the best course is to calcine in a scorifier or crucible, taking great care, during the process, to prevent clotting by keeping the temperature low, as the ore is very liable to fuse, by which means the antimony is oxidized, and in a great degree passes off in the state of vapour as antimonious acid (SbO^3). The calcined ore is rubbed down with coke-dust or anthracite-powder, and recalcined. The calcined ore is subsequently fused for coarse copper, with the addition of more carbonate of soda, and less borax than usual. If the ore is poor after calcination, it must be fused for regulus with the addition of iron and sulphur, &c., in the usual manner.

Arsenic.—If present in *grey* ores, they should be treated in the same way as for antimony. If it exists as mispickel, arsenical iron-pyrites, &c., the ore may be partially roasted, or treated with nitre on fusion for regulus. When present in the regulus, the latter, after calcination, should be mixed with some coke-dust or coal-powder, and re-calcined in order to reduce the basic arseniates always formed during the roasting process, and so to expel the arsenic as completely as practicable.

Methods of Estimating Copper by Wet Assay.

There are various processes described for the determination of copper by wet assay, *i. e.* by the aid of liquid reagents, but few of them are applicable to the estimation of copper in copper-ores, as they would occupy too much time, or are unsuitable for practical purposes. Wet methods yield more accurate results than can be obtained in the *dry* way, and it matters not which of the various methods is employed, or in what part of the world the assay is made; provided the sample is correctly taken, the results will closely agree, and this certainly cannot be always affirmed of the dry methods of assay. In this work those wet processes only will be noticed which by long experience in the Metallurgical Laboratory have been found best for practical purposes.

Sampling.—After the sample has been prepared, as for dry assay, a small quantity of the ore, say about 100 grs., should be taken out, and reduced to a finer powder than for dry assay.

Quantities to be taken for assay :—

Ores, &c., containing over	30	per cent. of copper	10 grs.
Ores containing from	4 to 30	,, ,,	20 ,,
Ores under	4	,, ,,	50 ,,

The balance used for weighing should be capable of carrying 500 grs., and of turning with $\frac{1}{100}$th of a grain. A chemical balance is the one usually employed. It should have a light counterpoised silver, platinum, or porcelain dish attached to it, in which the ore should be weighed out.

By Cyanide of Potassium.—This process was first made known by Mr. Henry Parkes in 1851, as applicable to the assaying of copper-ores. It has since been extensively used in South America (the ores consisting chiefly of oxides, carbonates, silicates, and oxychlorides), where it has almost superseded the method of precipitation by iron. It has also been applied in this country for the estimation of copper in slags, &c.; but as the copper-ores are bought and sold in England according to the return by dry assay, it has been somewhat limited in its application. Of all the wet processes by means of standard solutions, at present known, it is certainly the best adapted and most direct for assaying copper-ores, as the presence of iron does not interfere with the process, and in the greater number of instances filtration is unnecessary. Like all other methods, it requires experience to be skilfully conducted; but that it is capable of yielding correct results, within 0·1 or 0·2 per cent., has been fully proved by some thousands of assays, made by various persons, which have come under our notice during the course of several years, results very closely approximating having been obtained by different manipulators with the same samples of ores. Some difficulties will always be met with in taking up any new process, but no process should be condemned by an operator because he fails to succeed in his first trials.

When a solution of cyanide of potassium is slowly added to a blue ammoniacal solution of copper, the latter gradually loses its colour, and finally becomes quite colourless; upon this reaction, the estimation of copper by cyanide of potassium depends. By ascertaining, by direct experiment, the amount of cyanide of potassium solution required to discharge the colour in an ammoniacal solution containing a given weight of copper, it is easy, by a comparative experiment, to determine the amount of copper in a given weight of ore.

This process will be considered under the following heads :—Apparatus, Standard Solution, and Mode of conducting the Assay.

Apparatus.—It will be unnecessary, under this head, to enter into any detail in reference to the ordinary apparatus in common use in chemical laboratories, such as flasks, beaker-glasses, funnels, &c. The number of each will be regulated by the number of assays it is required to conduct at one time. The only special piece of apparatus necessary for the assay by standard solution is a *burette*. That usually employed in this country is known as the English burette or alkalimeter. It

should be about 18 inches high, ½ an inch in internal bore, ⅛ths of an inch in external diameter, of 1000 grs. capacity, and graduated to 200 divisions. When a number of assays have to be done at the same time, those known as Mohr's burettes are the best. Fig. 121 represents one of 1000-grain capacity, and graduated to 200 divisions, fitted up on a stand to facilitate manipulation. Into the upper part is fitted a cork, through which passes a piece of quill glass tubing, which may be used to connect the burette, by means of a piece of vulcanized India-rubber tubing, with the bottle or jar containing the standard solution, so that it may be easily filled. To the lower part of the burette a piece of glass tubing drawn out to a point is connected by means of vulcanized India-rubber tubing, and the flow of the standard solution can be regulated with the greatest nicety by means of a pressure-screw (see fig. 121, *b*) operating on this connecting piece of India-rubber tubing. The burette can be raised or lowered by means of the arms and screws attached to the upright pillar of the stand. The number of such burettes must be regulated by the requirements of the assayer. Any number of assays can be conducted at one time by one person by the aid of these burettes, of which several may be fitted up on one stand; or they can be attached to the table by means of bracket-arms.

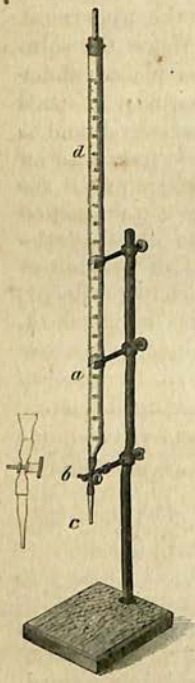

Fig. 121.

Standard solution.—2000 grs. of cyanide of potassium are to be dissolved in 4 pints (35000 grs.) of water. This salt is deliquescent, and should not be left exposed to the air. It is very soluble in water, and the solution is ready for immediate use. The above quantity will produce a standard solution, of which 1000 grs. will be equal to about 10 grs. of copper. That known as gold or photographic cyanide is the best, as the solution prepared from it may be kept for a great length of time without becoming discoloured. If common cyanide of potassium is used, about 2880 (6 oz. Troy) will be required for 4 pints of water. The solution prepared from it can only be kept for a few days without becoming discoloured and muddy; but when the solution is rapidly consumed, it answers very well for assay purposes.

An objection raised against the use of cyanide of potassium for standard solution is its liability to decompose. When numerous assays have to be made, this circumstance is not of any material consequence, as decomposition and consequent alteration of the standard take place very slowly. For instance, a large quantity of solution, prepared and used from time to time in assaying, had the following standards:—

Oct. 26th, 1858	1000 grs.	=	10·06 grains of copper.
July 25th, 1859	1000 ,,	=	9·84 ,, ,,
March 20th, 1860	1000 ,,	=	9·45 ,, ,,
June, 1860	1000 ,,	=	8·92 ,, ,,

From this it will be seen that it requires a considerable time to make any decided alteration in the strength of the solution. For practical purposes, the standard will not require checking more than once a week. The solution should be kept in bottles of green glass; lead glass bottles should be avoided; even the green glass bottles are slowly acted on by it, the glass being decomposed, and a thin scaly deposit formed.

The solution of cyanide of potassium is standardized as follows:— Three pieces of pure electrotype copper, previously cleaned by means of hydrochloric or dilute nitric acid, washed and dried, are accurately weighed. The weight of the pieces may vary from 5 to 10 grs. each. Each piece is dissolved in a pint flask by dilute nitric acid, and the solution is boiled to expel all nitrous acid fumes; it is diluted with water to about half-a-pint, and treated with ammonia in excess, when it will become deep blue. The burette is filled to the uppermost division, with the solution of cyanide of potassium. When the solution of copper is quite cold, the flask containing it is placed under the burette, and the solution of cyanide is allowed to run in in small quantity at a time, until the blue colour is almost discharged, and is replaced by a faint lilac tint. The number of divisions is then read off on the burette of solution of cyanide which has been required for decolorization. The second and third pieces of copper are proceeded with in exactly the same manner; and from the data obtained the amount of copper, equal to 1000 grs. of the solution of cyanide of potassium, is calculated according to the result of each experiment, and the mean of the three results is taken: this will be the standard. The following tabular form, from results actually obtained, will show how the data should be recorded:—

No.	Weight of copper taken.	No. of divisions of solution of cyanide of potassium required.	Calculated amount of copper 200 divisions (1000 grains) of standard solution is equal to.
1	5·055 grains	100·0	10·110
2	6·745 do.	132·5	10·181
3	5·155 do.	101·0	10·208
		Mean result or standard...	10·166

If the first two results agree, it may be unnecessary to obtain a third. Instead of calculating the standard as above, the calculation may be made so that the number of divisions of solution, equivalent to 10 grs. of copper, is used as the standard for estimating the percentage of copper in the ore.

Method of Assay.—A known weight of the ore is placed in a flask, or beaker-glass provided with a glass cover, and moistened with strong sulphuric acid; strong nitric acid is then added, and the whole is digested at a gentle heat, nitric acid being added cautiously from time to time, until *nitrous acid fumes cease to be given off*. The solution is diluted with a small quantity of water, and reheated; when the ore is completely decomposed the contents are transferred without filtration

into a pint flask, and diluted with water to about ½ or ¾ of a pint; excess of ammonia is next added, and the solution is allowed to become *quite cold*. When cold, without regarding the amount of hydrated sesquioxide of iron which may be present, the standard solution of cyanide of potassium is *gradually and cautiously* added in small quantities at a time, with occasionally shaking the copper solution, until the blue colour is nearly discharged, and there remains only a faint lilac-tint. The number of divisions required to produce this effect is read off, and from the standard the per-centage of copper is calculated. *Example*:— 200 divisions of the burette equal 10 grs. of copper; 20 grs. of the copper-ore required for decolorization 105 divisions; therefore—

Divisions.		Divisions.		Copper.		Copper.
200	:	105	: :	10	:	5·25

and $5 \cdot 25 \times 5 = 26 \cdot 25$ per cent. of copper.

The decolorization of the solution should take from ½ to ¾ of an hour for completion, according to the amount of copper present. The cyanide being added very slowly, especially towards the end of the process, the last tint should remain permanent, or nearly so, for about 10 minutes. To aid in recognising the tint of the solution a white glazed tile or piece of white paper should be placed under and behind the flask during decolorization. When the ore is a sulphide, with ordinary precaution it will be completely oxidized by sulphuric and nitric acids; but if any globules of sulphur remain they can be easily picked out after the dilution of the solution, ignited, and the residue, if any, digested in nitric acid, and added to the bulk of the solution. If any difficulty is experienced in dissolving the basic sulphates formed, some hydrochloric acid may be added with advantage. When silver is present, it must be got rid of by adding hydrochloric acid and filtering off from the residue.

When sesquioxide of iron is present, it imparts a greenish appearance to the ammoniacal solution, and the proper tint of the solution is best observed by placing the eye on a level with the top of the liquid; after a little practice the alteration in the tint of the oxide of iron which occurs will afford a sufficient indication until near completion, the reddish-brown colour becoming more distinct as the assay is proceeded with. If any difficulty is experienced in observing the tint towards completion, the precipitate may be removed by filtration. When the assay is finished the sesquioxide of iron will be free from copper, as the portion at first retained passes out into the solution during the course of decolorization. The sesquioxide of iron should not be filtered off in the assay, as it would retain a considerable amount of copper, which could not be perfectly extracted from it even by means of strong ammonia. By the cautious addition of cyanide of potassium to an ammoniacal solution of copper mixed with sesquioxide of iron, the latter may be wholly deprived of copper. After the copper has been determined, the sesquioxide of iron is filtered off, washed, dissolved in hydrochloric acid, reduced by zinc to the state of protochloride, and the amount of iron estimated by means of a standard solution of bichromate or permanganate of potash.

Interference of other metals.—The following experiments have been made on this subject. The copper was dissolved in the usual way in nitric acid, diluted with water to about ½ a pint, and ammonia added in excess to the solution. In each case the amount of solution of the foreign metal added contained at least 5 grs. of the metal.

Weight of Electro-type Copper taken.	Estimation made in the presence of	Remarks.	Number of Grains of Solution of Cyanide of Potassium required.	Calculated amount of Copper 1000 Grains of Standard Solution is equal to.
Grains.				Grains.
5·345	... ...	... ...	910	5·873
5·675	... ...	... ...	960	5·910
4·230	... ...	... ...	720	5·875
6·305	Sesquioxide of iron	Added as sesquichloride before the addition of ammonia	1070	5·890
8·150	Lead, antimony, tin, & bismuth	Added as chlorides before the addition of ammonia	1350	5·960
10·735	Do. do.	Do. do. do.	1800	5·960
6·645	Nickel.....	Added as sulphates before the addition of ammonia, there was no precipitate formed by the addition of the cyanide, and the solution was not decolorized, but remained yellow after the addition of 1630 grains of solution.....	...	...
6·410	Cobalt.....	Added as chloride before the addition of ammonia, a precipitate was produced during the experiment, but the solution was not decolorized by 2000 grains of standard solution	...	...
6·90	Antimony	Added as chloride	1160	5·948
5·30	Bismuth	Added as chloride, the precipitate formed on dilution re-dissolved on the addition of the ammonia	910	5·810
5·955	Lead	Added as chloride, no precipitate during decolorization	1020	5·838
5·335	Tin	Added as chloride, the precipitate by ammonia nearly all dissolved, leaving an opalescent solution	910	5·863
4·700	Arsenic	Added as arsenic acid	790	5·974
5·450	Silver	Added as precipitated chloride, the cyanide of potassium acts upon it during decolorization ...	...	...
3·955	Silver	Added as nitrate, interferes, as in the above experiment	...	...
3·895	Zinc.....	Added as chloride, the solution was decolorized by 1300 grains of solution, and the ammoniacal solution became turbid towards the close of the experiment.....	...	...

From the above experiments it will be seen that the metals which cause any material interference are silver, nickel, cobalt, and zinc. Certain precautions must be observed in the presence of the following metals:—

Iron does not interfere, when present as sesquioxide, except mechanically; the presence of a very large quantity somewhat prolongs the assay by the time occupied in the precipitate subsiding sufficiently to observe the tint of the solution. When present as arseniate it is soluble in ammonia, and in the presence of copper forms a brownish green solution: this can be easily remedied by the addition of some solution of sulphate of magnesia, when the magnesia combines with the arsenic acid, and the solution, after the lapse of a few minutes, acquires the proper tint. The assay can then be proceeded with, without filtration, in the usual way.

Manganese is seldom present in copper-ores in sufficient quantity to interfere. If present, it may be completely precipitated as peroxide by the addition of carbonate of ammonia and a few drops of bromine, and heating the solution, or allowing it to stand some time. When cold the assay can be proceeded with.

Nickel and cobalt.—Their presence is generally detected during the assay by the solution remaining of a yellowish tinge after the blue colour has disappeared by the addition of the cyanide of potassium. When present the copper must first be separated by precipitation.

Zinc.—It very often exists in copper-ores in the form of blende. It gives no indication of its presence during the assay. When present it is first converted into cyanide by the cyanide of potassium, before the copper is acted on, and the degree of this interference is pretty constant for a given weight of zinc: thus a quantity of standard solution of cyanide of potassium equivalent to 1 grain of copper would be equal to about 3½ grs. of zinc. Attempts have been made to estimate zinc by colouring the ammoniacal solution by means of a small quantity of solution of copper of known strength, and then adding the solution of cyanide until decolorization occurred; but the standard solution of cyanide in this case requires to be made so weak that the results were not satisfactory.

Arsenic.—It does not interfere except when present with iron.

Silver.—It interferes, but is easily got rid of by the addition of a few drops of hydrochloric acid, and filtration before the addition of the ammonia; the precipitation of chloride of silver is much promoted by shaking or the application of heat.

Lead, tin, antimony, bismuth, do not interfere.

When zinc, nickel, and cobalt are present, the copper must first be separated: this may be effected by—

a. Precipitation by means of a piece of iron from the dilute sulphuric acid solution, nitric acid being absent; redissolving the precipitated copper in nitric acid, diluting with water, &c., and estimating by the cyanide of potassium.

b. Passing sulphuretted hydrogen through the acid solution, filtering and redissolving the precipitated sulphide of copper in nitric acid, &c.

c. Precipitating the copper by hyposulphite of soda, and dissolving the disulphide of copper in nitric acid, &c., and estimating by the cyanide. This method is the quickest and best: the first, however, is a useful practical method.

By precipitation with hyposulphite of soda.—The ore is decomposed by boiling in the usual way by means of sulphuric and nitric acids; the solution is diluted, filtered, and washed; after filtration, the liquid, in quantity from ½ to ¾ of a pint, is heated to boiling; solution of hyposulphite of soda is then cautiously added in small quantities, when after a few seconds it will rapidly darken; and if sufficient hyposulphite has been added the whole of the copper will be precipitated as disulphide of copper, mixed with free sulphur, and with the evolution of sulphurous acid. The heat is continued, and if the whole of the copper is thrown down from the solution the precipitate will coagulate as it were, and separate easily from the supernatant liquor; and a white precipitate of sulphur will be produced on further addition of the hyposulphite. The whole is thrown on a filter while hot, and the precipitate is washed with hot water and dried; when dry it is carefully removed from the filter, without detaching any portion of the paper; the filter with adhering particles of the precipitate is ignited, and the residue added to the dried disulphide of copper; the whole is then heated in a covered porcelain crucible, placed over an air-gas-burner, until the excess of sulphur ceases to burn round the upper edge of the crucible. When cold the crucible and contents are weighed, and the weight of the former deducted. The disulphide should have a dull greyish black colour. If any doubt occurs as to the state of the residue, it may be re-ignited in admixture with sulphur, and weighed again. The amount of ash from the filter is subtracted, and from the weight of the disulphide of copper the amount of copper is calculated. 100 parts of disulphide of copper contain 79·85 parts of copper. If any black oxide remains with it, it is of no consequence, as it contains the same amount of copper as the disulphide, and therefore will not interfere with the result. After weighing, the disulphide should be tested to see that other metals are absent. This method may be used for separating copper from nickel, cobalt, zinc, manganese, &c. We have employed it for several years past. Hyposulphite of soda has been used in the quantitative estimation of copper in this country during several years, although the process has only recently been described by Fresenius.

In assaying ores consisting chiefly of copper or iron pyrites, instead of treating the ore direct with acids, after weighing, it may be partially roasted in a porcelain capsule in a muffle, or over an air-gasburner for about 10 minutes, by which means a large proportion of the sulphur will be driven off. The roasted ore is subsequently boiled in nitric acid during 20 minutes or ½ an hour, when the copper will be dissolved out, a portion of the oxide of iron remaining insoluble. Where a large number of assays have to be made, this mode is sometimes resorted to for the purpose of economising nitric acid, as the whole of that portion of acid which would be decomposed in the oxidation of the sulphur is thereby saved. It also obviates the trouble occasioned, sometimes, from the globules of sulphur remaining after prolonged boiling of the ore in nitric acid direct. The fact of a portion of the iron being left after calcination and boiling in nitric acid, as insoluble oxide, is

advantageous, especially in assaying by the cyanide method. The quantity of copper retained, if any, in the residue amounts to a mere trace, if the ore has been properly treated.

In assaying some poor copper-ores, where the copper is diffused through a large quantity of gangue, as in clay-slate, &c., it is sometimes difficult, if not impossible, to get out the last portions of the copper by means of acid; in this case the ore may be calcined, and then fused with bisulphate of potash, &c., and the estimation afterwards proceeded with in the usual way. This plan may also be employed for determining the copper in slags.

By way of illustration the following results by different methods, and obtained by different persons with the same ore, are appended:—

Iron pyrites containing copper pyrites gave—	Copper per Cent.
By boiling the ore in nitric acid and estimating the copper direct by cyanide of potassium (by R. Smith)	6·04
By calcining the ore previous to boiling in nitric acid (by R. Smith)	6·057
By precipitation by hyposulphite of soda, and weighing as disulphide (by Mr. C. Tookey)	6·02
By cyanide of potassium, by another person	6·12
By cyanide of potassium, by a third person	5·98
By dry assays	5·80

By a standard solution of hyposulphite of soda.—This process was first described by Mr. E. O. Brown,[6] and is extensively used for the determination of copper in gun-metal, &c., at the chemical department of the Royal Arsenal, Woolwich. It is especially adapted for the estimation of copper in commercial varieties of copper, bronze, &c., where lead or iron is not present in large quantity. It requires some modification to render it applicable to the assaying of copper-ores. The process is founded on the reaction between iodine and hyposulphurous acid, when the products are hydriodic and tetrathionic acids. The completion of the reaction is manifested by the bleaching effect produced upon a solution of starch added during the time of experiment. Slight differences of temperature, or variations in the mode of manipulation, do not in any way affect the results. For experiments upon this subject, the paper before alluded to should be consulted.

The reagents required are—1. A solution of hyposulphite of soda. This is made by dissolving 1300 grs. of the crystallized salt in 4 pints of water, and standardizing by means of weighed pieces of pure electrotype copper by the process hereafter described, the mean results being taken as the standard.

2. Iodide of potassium. The salt may be used in crystals, and should be free from iodate of potash.

3. Solution of starch. This is prepared by boiling starch in a large quantity of water, and allowing it to stand until the insoluble residue has subsided; the clear supernatant liquor, which may be decanted off, is employed.

[6] Quarterly Journal of the Chemical Society, April, 1857.

Process.—From 8 to 10 grs. of the copper or alloy are dissolved in dilute nitric acid, and the nitrous acid is expelled by boiling. To the solution, diluted with a small quantity of water, carbonate of soda is added until a portion of the copper remains precipitated. The solution is treated with an excess of pure acetic acid, and poured into a pint-flask, when it is further diluted with water. About 60 grs. of iodide of potassium are dropped into the flask and allowed to dissolve. The standard solution of hyposulphite of soda is now poured in until the greater part of the pure iodine disappears, and the solution acquires a yellow colour. A little of the starch solution is now added, and the addition of the hyposulphite of soda cautiously continued until bleaching is completed, or, in other words, until the solution becomes colourless. The number of divisions on the burette containing the standard solution is read off, and the amount of copper calculated therefrom.

As iron is generally present in copper-ores, and the red colour of the acetate of iron renders it somewhat difficult to observe the reaction of the hyposulphite during the process, in order to make the process applicable to the estimation of copper in copper-ores, it is necessary, after having decomposed the ore, &c., and expelled the nitrous acid, to dilute and filter, precipitate the copper from the filtrate by hyposulphite of soda, and redissolve the precipitated disulphide of copper in nitric acid. The copper may then be estimated in the manner described.

When iodide of potassium is added to the acetic acid solution of protoxide of copper, di-iodide of copper is formed, with the liberation of an equivalent amount of free iodine which dissolves in the excess of iodide of potassium present, the potash combining with the acetic acid. By the addition of the standard solution of hyposulphite of soda, the free iodine is converted into iodide of sodium, with the formation of tetrathionate of soda. The starch solution merely serves to render the termination of the reaction manifest, the blue iodide of starch first formed becoming gradually bleached as the process approaches completion. The reaction may be expressed by the following formula :—

$$2(CuO, \bar{A}) + 2KI = Cu^2I + I + 2(KO, \bar{A})$$
$$I + 2(NaO, S^2O^2) = NaI + NaO, S^4O^5$$

COLORATION-TEST.—A ready method of approximately determining the proportion of copper in slags containing only a small quantity of the metal is of much use. Even in the best-conducted copper-works it is desirable that the *ore-furnace slag* should be occasionally examined chemically as to its content of copper; and the smelter should not always be satisfied that it is sufficiently *clean* when he fails to discover any sensible amount of regulus in shots on its freshly fractured surface. The blue coloration-test by ammonia may be conveniently adopted for this purpose. A series of bottles of colourless glass, and of precisely the same capacity, must be procured, and their form should be quadrangular in preference to cylindrical. These bottles are filled with dilute standard solutions of copper dissolved in excess of ammonia. In the first bottle there should be, say $\frac{1}{16}$ of a grain of copper,

in the second $\frac{2}{10}$, in the third $\frac{3}{10}$, and so on. The intensity of the blue coloration will be proportionate to the amount of copper in the bottles. In testing a slag, it should be reduced to fine powder, and digested with nitro-hydrochloric acid; and when the decomposition is complete, the solution should be diluted and poured into an empty bottle of precisely the same capacity and shape as those of the series containing the standard ammoniacal solutions of copper. Should it be desired to separate the silica, the process usually employed in an analysis must be resorted to. The slag, in a finely divided state, is digested with hydrochloric acid until it is completely decomposed, and then the whole is evaporated to dryness; hydrochloric acid is poured on the dry residue, and, after the lapse of about half an hour, a little nitric acid or chlorate of potass is added to peroxidize the iron. The silica may now be easily separated by filtration, and the filtrate treated as above described. Ammonia in excess should be added, and the bottle filled up with water, so that there may be the *same volume* of liquid as in one of the test-bottles. This solution, with respect to intensity of colour, is now to be compared with those in the test-bottles; and from that with which it most nearly agrees the amount of copper is deduced. It is requisite that the solutions should be very dilute, for otherwise the colour is so intense that no difference can be remarked even in solutions containing very different proportions of copper. Any person who has had slight experience in chemical manipulation will be able, after a few preliminary experiments, to construct a series of these test-solutions as may best suit his convenience. It need hardly be remarked, that in applying the coloration-test the bottles should be placed in a good light between a side window and the observer. It is not necessary to filter the solution after the addition of the ammonia, provided time be allowed for the complete subsidence of the precipitate of sesquioxide of iron formed. A sensible amount of copper is retained by the sesquioxide of iron, from which it cannot be separated even by a great excess of ammonia. The presence of oxides, such as those of nickel, cobalt, &c., which dissolve in ammonia, producing coloured solutions, will render this method of testing inaccurate.

Le Play appears to claim the merit of having first suggested the coloration-test for copper-slags, &c. He thus writes: "After numerous trials, I have been led to the following process, ... which leaves nothing to be desired with respect to rapidity of execution:— The principle of this process consists in judging of the quantity of copper contained in a liquor by the intensity of the blue tint which protoxide of copper (CuO), dissolved in ammonia, communicates to a given quantity of water."[7] Now, Heine in 1839 published a description of this identical process, which he had employed in determining the amount of copper in slags;[8] but Le Play's description of it did not appear until nine years afterwards. Mr. Keates informs me that he had used it so long ago as 1830.

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[7] Procédés Métallurg., p. 454.

[8] Methode zur Ermittelung des Kupfergehalts aus Schlacken. Bergwerksfreund, 1839. 1. p. 33.

Inaccuracy of the Cornish method of dry assaying.

This is a tender subject with copper-smelters. The fact is, that in the Welsh process of smelting a larger quantity of copper, or *surplus*, is obtained than is indicated by the *produces* of the Cornish assayer, that is, exclusive of the copper obtained from the *one hundred weight* of ore in excess of the ton of 2240 lbs. (see p. 306), which, in former days, was supposed to be lost in transit from the mines! and the amount of this *surplus* is regarded by the smelters as a trade secret. Whatever profit may have been derived from the *surplus* in what some smelters now designate as the *palmy* days of copper-smelting, it is certain that it cannot now be properly regarded as any special source of profit; because it is an essential element in the consideration of the *prices* of ores, and is, accordingly, paid for by the smelter. In the present day the miner would not generally receive a farthing more for his ore, whatever changes might be effected in the plan of assaying and the mode of sale. Miners believe that they are cruelly victimized by the smelters, and often entertain the fallacious notion that if they could only smelt their own ores their dividends would greatly increase. Smelters consider it desirable to keep miners as much in the dark as possible, and so suspicion of unfair treatment on the part of the former is engendered in the minds of the latter. My impression is—I may be mistaken—that there would be a much better understanding between miners and copper-smelters if copper-ores were assayed by a more accurate method than the Cornish, and sold at a given sum per unit (say 1 cwt.) of copper in the ore, according to the market value of copper at the time.

I will now proceed to establish the fact that the *produce* obtained by the Cornish method, however skilfully it may be conducted, is always sensibly below the actual amount of copper in the ore. When at Swansea in 1859, I was anxious to procure portions of the samples of ores which had been supplied to the smelters from the ore-yards prior to a sale at Swansea on a particular day. In my innocence I did not for a moment conceive that any smelter would object to furnish me with the residues of the identical samples which had been operated upon by his private assayer; and accordingly I applied for some of these residues to certain smelters whom I have long had the pleasure of numbering amongst my personal friends. Great was my surprise when I met with a distinct refusal, on the ground that, being members of the Association, they were pledged to inviolable secrecy in *everything relating to assays;* but the refusal, I should observe, was accompanied with every courteous expression of regret. Nay, in my utter ignorance, at the time, of the pledge of secrecy, I had even ventured to ask for the produces rendered by the Association assayers! (see p. 307, ante). In spite of these unexpected obstacles, I am happy to state that I have succeeded in honourably procuring all the information which I needed, or even desired. Captain Petrie and other gentlemen connected with the ore-yards of Swansea have provided me with samples of all the parcels of ores, &c., sold at Swansea Nov. 15, 1859, the sampling having taken place on the 6th of October preceding. Out of these samples a series has been selected for examination in the Metallurgical

TABLE OF COMPARATIVE RESULTS BY THE CORNISH AND WET METHODS OF ASSAYING.

No.	MINES.	NATURE OF THE ORE, &c.	DRY ASSAY, CORNISH METHOD.		WET ASSAY.			Excess of produce of mean of wet assays over produce of Associated Smelters.	Deficiency of produce of assays of Associated Smelters, calculated on 100 parts of copper.
			Sellers' Produces.	Associated Smelters' Produces.	Percentage of copper determined by R. Smith.	Percentage of copper determined by W. Weston.	Mean Percentage of copper by wet assays.		
I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.	X.
1	Cuba . . . . *Golconda*	Copper pyrites, iron pyrites, quartz, &c. .	11⅝	11⅓	11·80	11·90*	11·85	0·35	2·95
2	Do. do.	Do. do. . .	11¼	11½	11·80	12·01*	11·90	0·40	3·36
3	Do. do.	Copper pyrites, quartz, &c.	21⅞	22	22·34	22·46*	22·40	0·40	1·78
4	Do. do.	Do. do. . .	25½	25¼	26·10	26·50*	26·30	1·05	3·99
5	Cobre . . . *Henrietta*	Do. do. . .	12⅝	13	14·12	14·18	14·15	1·15	8·12
6	Do. do.	Do. do. . .	12⅞	12¾	13·47	13·45	13·46	0·71	5·27
7	Do. *Catherine Rosser*	Do. do. . .	12¼	12¼	13·87 [1]	14·08	13·97	1·72	12·31
8	Bearhaven . . *Allihies*	Do. do. . .	9½	9⅜	11·08	10·86 [3]	10·97	1·60	14·58
9	Do. *Swansey*	Do. do. . .	10½	10⅜	13·22	13·07	13·14	2·39	18·18
10	Springbok . . *Texian*	Do. do. . .	36½	35½	38·51	38·65*	38·58	3·08	7·98
11	Do. do.	Do. do. . .	36¼	35⅝	38·76	38·43	38·59	3·09	8·00
12	British Regulus . *Dart*	Consists chiefly of iron, sulphur, and copper	16⅜	15¾	18·37	18·47	18·42	2·67	14·49
13	Ookip . . . *Texian*	. . . . .	34	34	37·25	37·28	37·27	3·27	8·77
14	Do. do.	. . . . .	31	31½	33·00	32·71	32·86	1·61	4·90
15	Bampfylde *Ann Elizabeth*	Grey copper ore, with hæmatite . . .	15¾	16⅛	17·75	17·45	17·60	1·48	8·52
16	Spanish *Catherine Rosser*	. . . . .	2½	2⅞	3·40	3·51	3·46	0·59	17·05
17	Australian Regulus *Rail*	Consists chiefly of disulphide of copper, with some sulphide of iron	64⅜	62	67·55 [2]	67·28	67·41	5·41	8·03
		General Average	21½ / 21·46	21⅓ / 21·26	23·081	23·076	23·079	1·82	8·72

[1] Mean of two assays by process *a*. (1.) 13·93. (2.) 13·81.
Do. do. do. (1.) 67·60. (2.) 67·50

[2] Mean of two assays { (1.) by process *b*. 10·90 / (2.) do. *c*. 10·81.

Laboratory. The *whole* of each sample was dried and reduced to impalpable powder, and portions were assayed with the *greatest possible care*. The results will be found in the accompanying table. In the 2nd column the word in italics is the name of the vessel in which the ore was imported. In the 4th column are the produces of the sellers, as published in the 'Swansea Ore Circular' for Nov. 15, 1859. In the 5th column are *the produces of the Association Assayers*, which are supposed to be kept impenetrably secret. I have received these results with permission to publish them. I am not indebted for them to any smelter, or any person in the employ of any smelter, or to any assayer. The fact of my possessing them will satisfy the members of the Association that, in accordance with the old belief, secrets which are known to many have but little value, and might as well be known to all. In the 6th column are the percentages of copper determined by my colleague, Mr. R. Smith, who conducts our Assay Laboratory, and has during the last ten years had almost daily practice in assaying: all the results were obtained by the process *a*, described further on. In the 7th column are the percentages of copper determined by a former student of our School of Mines, Mr. W. Weston, who has been constantly engaged for two years in analytical work in the Metallurgical Laboratory. The produces marked * were obtained by process *b*, and the rest by process *c*, now to be detailed.

a. The ore was decomposed by sulphuric and nitric acids: the solution was diluted with water, and then treated with ammonia in excess. The copper in this ammoniacal solution was estimated by a standard solution of cyanide of potassium, according to Parkes's method.

b. The ore was decomposed by sulphuric and nitric acids; the solution was diluted with water and filtered; hyposulphite of soda (NaO, S^2O^2) was added to the filtrate; the disulphide of copper, thus precipitated, was dissolved in nitric acid; the solution was treated with excess of ammonia, and the copper in this ammoniacal solution was determined by Parkes's method.

c. The ore was decomposed as above, and the copper precipitated as in process *b*; but the disulphide of copper, after solution in nitric acid, was precipitated by potash and weighed as protoxide.

It will be perceived from the figures at the bottom of the 10th column that on the average the smelters receive 100 tons of copper, when the Cornish method of assaying would lead to the conclusion that they receive only 91·28 tons; but it must be remembered that there is a considerable and inevitable loss of copper in smelting. The *surplus* which the smelters have been accustomed to expect from their furnaces, beyond the produce indicated by the Cornish method, is about 9 per cent.; but part of this excess is derived from the hundred weight of ore which they obtain in addition to the ton. The *surplus* deduced in the Table is 8·72 per cent.; but this deduction, it must be borne in mind, is made on the supposition that an equal quantity of each ore was sold at the sale in question, which was very far from being the case. The average excess of copper which the smelters actually receive must be much greater than 8·72 per cent.; for, in addition to the surplus of 9 per cent. which their furnaces should

yield, a large amount of copper is lost in the ore-furnace slag. Of late, I know that some disappointment has been experienced on account of this surplus having been sensibly below 9 per cent.; and this has been attributed to the large importation of *rich regulus*, &c., in assaying which by the Cornish method there is proportionately less loss of copper than upon poorer ores or products. It is, however, not a little singular that there should be so great a difference as 5·41 between the results of the Cornish method and those of wet processes in a regulus containing more than 60 per cent. of copper, like that of No. 17 of the Table. Perhaps the Association Assayers may have heard expressions of disappointment regarding the decrease of the *surplus*, and have considered it proper to make a certain reduction from the produces actually obtained by them from rich cupriferous substances of this nature, on the ground that the surplus *ought* to be regarded as a *constant quantity*.

TABLE OF THE RESULTS OF ASSAYS BY THE CORNISH AND WET METHODS OF A SERIES OF COPPER-ORES OCCURRING IN THE COPPER-SCHIST (KUPFERSCHIEFER), NEAR MANSFELD, PRUSSIA.

Produce per cent. by Cornish assay.	Produce per cent. by wet assay.	Excess of produce by wet assay over the Cornish assay.	Deficiency on 100 parts of copper by Cornish assay.
15⅞	20·19	4·31	21·35
7½	9·88	2·38	24·09
2½	4·97	2·47	49·29
3	5·68	2·68	47·18
1	2·53	1·53	39·52
3⅛	6·44	3·31	51·39
8	10·10	2·10	20·79
½	1·48	0·98	66·21

The Cornish assays were made by one of the most experienced Cornish assayers. Two wet assays of each sample of ore were made in the Metallurgical Laboratory, one by standard solution of cyanide of potassium by R. Smith, and the other by the hyposulphite of soda method by C. Tookey. The produces given in the table are the means of the two assays. Portions of the identical samples operated upon by the Cornish assayer were employed for the wet assays.

I am indebted for the information in the table subjoined to Mr. Edward Riley, who was for some time engaged in the Metallurgical Laboratory in the analytical investigation of the iron-ores of Great Britain.

No.	Nature of the Ore.	Produce per cent. by Cornish assay.	Produce per cent. by standard solution.	Produce per cent. by analysis.	Lead in 100 parts of ore.	Excess of produce of the mean of produces by *wet* assay and *analysis* over the Cornish assay.	Deficiency on 100 parts of copper by Cornish assay.
1	Yellow copper-ore	22⅜	25·04	24·92	1·77	2·60	10·41
2	Do.	8½	10·69	10·29	8·69	1·99	18·97
3	Copper mundic ...	2⅜	3·52	3·44	0·18	1·11	31·81
4	Do.	2⅛	4·86	4·92	4·30	2·76	56·23

The Cornish assays were made by Mr. Penrose of Redruth, and the other results were obtained by Mr. Riley. Portions of the *same pulverized samples* were employed both by Mr. Penrose and Mr. Riley. In the *wet* assays the ore was roasted, and the roasted product dissolved in hydrochloric acid; the solution was boiled with sulphite of soda to reduce the sesquichloride of iron to protochloride; the copper was precipitated by sulphuretted hydrogen; the sulphide of copper was dissolved in nitric acid; and the copper was determined by a standard solution of hyposulphite of soda and iodide of potassium, according to Brown's method. The produce by analysis was determined in the ordinary way, by precipitating the copper as protoxide by potash, &c. The produce of another sample of No. 4 was by another Cornish assayer, and reported to be 3¼ per cent.

Although the evidence already adduced is quite sufficient to prove that the Cornish method of assaying is inferior in point of accuracy to wet methods, yet I will add the following results, obtained in large sulphuric acid and soda works by the chemist engaged there, and who was formerly a student in the Metallurgical Laboratory.

Nature of the Substance Assayed.	Produce of copper per cent. by Cornish assay by Mr. Christoe.	Produce of copper per cent. by Cornish assay made at Swansea.	Produce of copper per cent. by standard solution of cyanide of potassium by the chemist of the works.	Excess of produce by wet assay over the Cornish assay.	Deficiency on 100 parts of copper by Cornish assay.
Regulus.....	10⅞	. . .	12·57	1·70	13·52
Do.	10⅛	. . .	11·54	1·42	12·30
Copper mundic.....	2⅞	. . .	3·14	0·27	8·59
Do.	0⅞	. . .	1·66	0·79	47·59
Do.	3⅛	3⅞	4·75	1·25	26·31
Do.	3¼	3⅝	4·59	1·15	25·05

While I am desirous of directing attention to the inaccuracy of the Cornish method of assaying, I am anxious that the motives by which I am actuated in so doing should not be misinterpreted by mine adventurers. It is far from my intention to lead them to infer that the smelters take advantage of the inaccuracy of this method, and do not in consequence pay a sufficient price for copper-ores. So far as I am able to judge, my conviction is that generally, in the present day at least, the ores are sold at their full value. I advocate the substitution of the least incorrect method of assaying, because I believe it would be to the advantage of all concerned. A moderately skilful and experienced manipulator may by means of wet methods of assaying determine the produce of a copper-ore with rapidity and certainty, and in the case of many ores with a degree of accuracy quite unattainable by the Cornish method, even when conducted by the most practised hands. With an assay-office properly arranged and organized for wet assaying, a large amount of work could be done in a short time, and less laboriously than by the dry way. The argument in favour of the Cornish method, that it approximately represents the actual furnace produce, or that the characters of the *prill* enable the smelter to predicate the

quality of the copper which he may expect to produce, is quite fallacious. In the first place, it would be just as easy to calculate the surplus from the exact result of the wet assay, inasmuch as it is regarded as a pretty constant quantity; and, in the second place, the fluxes employed in the crucible may in many cases produce effects to which there is nothing analogous in furnace operations on the large scale. Moreover, it is to the smelter's interest that he should at all times know as nearly as possible the actual content of copper in his ores, in order that he may be aware of the actual amount of loss in smelting and be prompted to use every effort to reduce that loss to a minimum.

Loss of Copper.

Absorption of copper in furnace-bottoms.—As the bottoms are composed of sand, they are necessarily porous and become impregnated with copper. The thickness of the bottoms was formerly much greater than at present, and, consequently, there was a proportionate infiltration of copper. The quantity of copper reported to have accumulated in the bottoms of some of the old furnaces seems almost incredible. I was informed on good authority in Swansea that not less than 65 tons of copper had been extracted from the bottom of a single furnace. In the Metallurgical Collection of the Museum of Practical Geology is a large and beautifully-crystallized piece of copper, presented by Mr. William Edmond, which was found under the bottom of a furnace at a depth of 14 feet below the surface of the ground! One of the principal smelters at Swansea informed me in 1848 that an ancestor of his had purchased old copper-works and obtained from the furnace-bottoms an amount of copper from which he realized far more than the purchase-money. I have received the following information on this subject from a practical smelter of great experience, on whose word I can place implicit reliance. In the course of working during some years an *ore-furnace* bottom of the usual dimensions adapted for melting a charge of 24 cwt. will absorb from 4½ to 5 tons of copper; a *fine-metal furnace* bottom will absorb from 7 to 8 tons; a *roaster-furnace* bottom about 10 tons; and a *refinery-furnace* bottom from 8 to 9 tons. A *refinery-furnace* with a *new* bottom may absorb as much as 5 tons of copper in working the first charge.

Loss of copper in smelting.—The annual total loss of copper in the Welsh process must be very considerable. It occurs chiefly in the ore-furnace slag, which, on the average, we have seen reason to believe, contains not less than 0·5 per cent. of copper. Those who have seen the prodigious accumulations of this slag at the copper-works of Swansea and the neighbourhood will have an accurate conception how great the loss must be, when they reflect that every 100 tons of the slag contain half a ton of copper. The green efflorescence so frequently present on the walls built of this slag bounding the road near the Hafod Works and elsewhere must often, one should think, excite unpleasant impressions in the minds of the great smelters as they travel along. Le Play estimates the loss of copper in the ore-furnace slag to be 2·8 per cent. of

the total copper obtained. Admitting that about 30,000 tons of copper are annually smelted in this country, it would follow that 840 tons of the metal are annually thrown away, or, in value, supposing the average price to be 100*l.* per ton, not less than 84,000*l.* worth.

In order to lessen the loss arising from the diffusion of shots of regulus in ore-furnace slag, Mr. Edmond suggested that it would be quite practicable so to dispose the ore-furnaces and arrange the periods of fusion as to allow the slag to be tapped, not skimmed off, from four furnaces into one pit; and, as there would thus be a large volume of melted slag, which would remain liquid in the interior for a considerable time afterwards, any regulus which might escape along with it from the furnace would subside and collect into a mass at the bottom.

Some copper may escape in the form of *copper-rain*, but the amount is, probably, very insignificant. My friend Sir William Logan, formerly a copper-smelter at Swansea, but during many years Director of the Geological Survey of Canada, informed me that at one smelting establishment at Swansea about a ton of copper-rain was annually collected from the roofs of the buildings over the furnaces, especially that of the refinery.

Another cause of the loss of copper is the escape of cupriferous particles in the currents of smoke from the various furnaces; but, according to the late Mr. Vivian, the loss arising from this cause is very small, "although, by the most absurd and exaggerated statements, it has been otherwise represented."[9] On this subject Le Play makes the following observations:—"I have ascertained that all the chimneys of the Welsh furnaces evolve pulverulent matters containing copper. These matters may be collected at the upper part of the highest chimneys, and upon the roofs through which these chimneys protrude. They are very rich in the roasting and refinery furnaces; even those in the chimneys of furnaces in which the poorest ores are calcined contain a notable quantity of copper. I have even had the opportunity of demonstrating the carrying away of this coppery dust under circumstances in which it could hardly have been suspected that this cause of loss could exist. The proprietor of Welsh smelting-works being desirous of condensing the sulphurous acid from the calcining furnaces, instead of sending it into the atmosphere, was led by the arrangement of his works to conduct the gases evolved during calcination through wide horizontal flues into a condensing apparatus at a distance of 100 metres (about 109 yards), and with the very feeble velocity of 0^{m} 70 (about 2ft. 3in.) per second. Nevertheless, even at this great distance from the furnaces, the condensing apparatus, which consisted essentially of a kind of artificial rain, occasioned the deposit of a considerable quantity of dust, which contained about 3 per cent. of copper, and which, analysed approximately, was found to be composed as follows:—

[9] Proceedings, &c., p. 19.

Protoxide of copper (CuO)	3·5
Sesquioxide of iron	22·0
Silica, alumina, lime, and magnesia	55·5
Arsenious acid, carbonaceous dust	19·0
	100·0

There is not much doubt that Le Play in the preceding statement refers to the late Mr. Vivian and the Hafod Works; and it seems also pretty evident that he estimates the loss of copper in flue-dust as greater than Mr. Vivian was disposed to admit. In the absence of positive data no satisfactory conclusion can be arrived at as to the probable amount of this loss; yet, from what I have seen of various smelting operations, I am inclined to the belief that it is not insignificant. During the process of calcination the pyritic ores decrepitate considerably, and much almost impalpable dust is produced, which may be readily carried off in the gaseous currents flowing through the furnace, though at a low velocity.

I am informed by a practical smelter of great experience, whose powers of observation I can trust, that the yield of copper is diminished by the presence of much fluor-spar in the ores, though the quality of the metal is generally very good. He had obtained satisfactory evidence on this point, especially from having smelted large quantities of ore from a well-known mine, the name of which, for obvious reasons, I must not disclose. Hence it would seem that a portion of copper may have been volatilized in the state of fluoride. On one occasion my informant introduced some *raw* ore from the mine above alluded to, when dense white fumes were emitted during the melting down of the charge, and the *metal* was brought *more forward* instead of being *thrown back*. Why this should occur I do not at present understand. We have previously considered how fluor-spar (CaF) may be decomposed under these conditions. Faraday, it will be remembered, detected hydro-fluoric acid in water which had been exposed to the smoke from the ore-calciner flue at the Hafod Works. There are many interesting metallurgical phenomena connected with fluor which have not hitherto been investigated. In copper-smelting in former times fluor-spar was, if I mistake not, generally added as a flux, though it is now but seldom expressly used with that object.

The copper in furnace-bottoms is not to be regarded as lost, as it is eventually recovered when the bottoms are broken up and melted down; yet in all operations of this kind a certain loss is inevitable.

At Åtvidaberg M. Malmqvist estimates the total loss of copper as about 0·25, or ¼ per cent. of the raw materials employed. The slags thrown away contain about 0·5, or ½ per cent. of copper, and may be taken at about half the weight, or 50 per cent. of the raw materials.

Commercial Details concerning Copper-Smelting.

Freights.—Freight from Cornwall for all descriptions of copper-ores was 3*s.* 6*d.* per ton, September 1859. Formerly this charge, inclusive of carriage from the mines to port, was 10*s.* per ton of ore delivered at the works; whereas at present these two charges average about 6*s.* 6*d.* per ton.

Freight of copper-ore from Cuba to Swansea varies from 2*l.* 10*s.* to 2*l.* 15*s.* per ton of 20 cwts. Freight from Callao, South America, has been as low as 1*l.* 16*s.*; in September, 1859, it was 3*l.* 5*s.*, and outward to the same port 1*l.* 17*s.* The Cuba freights are constant, and do not—like those from South America—vary with the price of copper. My authority for this information is Mr. Nicholson, who is largely engaged in the shipping trade between Swansea and South America.

Weights by which copper-ore is sold.—The ore is sold in England by the ton of 21 cwts. (of 112 lbs. to the cwt.—*i. e.* 2352 lbs. to the ton), estimated *dry;* but if it is imported from abroad, it is the custom to allow the buyer 2½ lbs. per 21 cwts., *i. e.*, 2376½ lbs. to the ton.

Cost of the Welsh method of copper-smelting.—There is reason to believe that metallurgical treatises and papers frequently contain statements as to the cost of production which are very erroneous, and may seriously mislead inexperienced persons. Not long ago it was gravely declared at a meeting of the Society of Arts, that the average profits of copper-smelting were not less than 40 per cent. on the capital; and during the present year (1861) advertisements have appeared in the 'Times,' under the sanction of respectable names, announcing the formation of a great Copper-Smelting Company with not less than 1,000,000*l.* capital, and inviting subscriptions on the ground that 30 per cent. profit might be reasonably anticipated. The scheme may have been put forth *bonâ fide*, but I doubt not that its promoters were mistaken in their estimate.

No reliable *general* estimate of the cost of *smelting* copper can be furnished, as it must of necessity vary with the ever varying cost of fuel, labour, iron, fire-brick, and other materials; and this variation applies even to any particular works at different periods, while scarcely any two works are precisely similarly circumstanced. Thus at one establishment fuel now costs nearly double what it did some years ago at the pit's mouth, and wages are at least 10 per cent. higher. Then the cost of smelting a particular kind of ore varies much with the circumstances of the smelter's stock: at one period calcination may be saved by fortunate concurrence of another description of ore; and not only so, but the admixture be productive of cleaner than ordinary slag. On the other hand, every process may have to be encountered, and the result as to slag may be unsatisfactory. Besides, there is the cost of pulling down furnaces and the breaking up of furnace bottoms, and the conversion of their contents into marketable copper, together with many other uncertain contingencies, constantly recurring in all large establishments of this nature, which make it impossible to offer a reliable general estimate. Nothing, in fact, short of an examination of a smelter's accounts would be any guide in a commercial point of view, and not even that unless the quantity of ore of each kind and its percentage of copper were set forth. But if the matter is looked at commercially, it will be perceived at once how little to be relied upon any such general estimate can be. Large quantities of copper-ore are bought at the mines and carried, at the smelter's expense, to a shipping port.

From one mine the carriage may be 3*s.* per ton, from another 10*s.*; then there is freight to the landing-place; and at one establishment the ore may be landed nearly at the furnace mouth, at another it may have to be transhipped into barges or loaded into railway waggons at an extra cost of some shillings per ton. Again, one smelter's furnaces may be near his market for copper, another's more distant, when transport becomes more costly. By way of example, it may be stated that in one case the cost of conveying copper to market, the cost of agency in selling it, and the discount allowed to purchasers for prompt payment, equalled the cost of making copper from some richer descriptions of ore.

Le Play has entered into elaborate calculations concerning the cost of smelting copper by the Welsh method; but, as it does not appear that he had access to the balance-sheets of the establishment in which he was permitted to study the process, the results at which he arrived cannot be received as authoritative. It seems hardly possible that any person—however perfect his knowledge may be of the theory and practice of copper-smelting, and however shrewd and expert he may be as an accountant—should be able to deduce with certainty the cost of production from the data which may be collected in works by personal inspection or elicited from workmen. From information on this subject which Le Play obtained at Swansea, he was led to conclude that copper-smelting might be profitably conducted at Caronte, near Marseilles; and, for various reasons which he enumerates, he advised the erection of copper-works in that locality. He, moreover, expressed an opinion that there was no other locality in Europe in which the metallurgical treatment of copper-ores by the *wet way* might be attempted with greater prospect of success.[1] In consequence of the publication of these opinions by Le Play, not fewer than four establishments for the extraction of copper were erected near Marseilles, known as the Usines de Caronte, de Rouet, de Septèmes, and de Bouc. The latter was destroyed in 1854, and in 1858 all had become defunct. The following comment appears in a notice of these works by Simonin.[2] "The particular position of Caronte had been indicated as the best for works in the south of France by an illustrious engineer, whose eminent talents have shed so great a lustre on the study of metallurgy, and especially on the metallurgy of copper —M. Le Play. But now the experience of years has destroyed illusions prematurely, perhaps, conceived, and the important problem of the treatment of copper-ores in France appears beset with difficulties (et la question avantageuse du traitement du cuivre en France parait environnée d'écueils) except, possibly, in cases altogether exceptional."

A method intermediate between the Welsh and Continental methods,

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[1] Procédés Métall., &c., p. 414.

[2] Notice sur les Usines à Cuivre et les Usines à Antimoine des Bouches-du-Rhône. Par M. L. Simonin, Ingénieur Civil à Marseille, p. 535. Bulletin de la Société de l'Industrie Minérale, 3. 4ième Livraison, 1858.

similar to that recommended by Le Play,[3] was practised at these works. Both blast and reverberatory furnaces were employed. A notice of the *wet* method, which was also tried at Le Play's suggestion, is given at p. 450.

Sir W. Logan's formula of the cost of copper-smelting.—Sir William Logan informs me that, when formerly engaged in copper-smelting, he ascertained with great care the exact cost of each operation, and deduced the following formula for calculating the total cost of the entire process with ores of varying produce, namely, 10 shillings per ton of ore, with the addition of 2 shillings for every unit, *i. e.* 1 per cent., of produce as determined by the Cornish method of assaying. This formula comprises all expenses from the purchase of the ore (exclusive of Cornish carriage) to the refining of the copper inclusive; and he assured me that he found it applicable to all ores without exception. But it is obvious that it must vary with the *price of labour and fuel;* and both these important items of expenditure have advanced considerably since the days when Sir William, in conjunction with Mr. Starling Benson, carried on the business of copper-smelting. In conversing with a copper-smelter not long ago respecting the formula in question, he expressed his opinion that with 1*s.* 9*d.*, instead of 2*s.* per unit of produce, a more correct estimate would be obtained. I have recently had the opportunity of inspecting an actual balance-sheet of one of the largest firms at Swansea, and I found that the formula, with the modification just mentioned, gave very nearly the same sum as charged in this balance-sheet for smelting costs. Supposing the average produce of the ores smelted to be 8 per cent., the cost of smelting 1 ton of copper will be

$$\frac{100 \times 10 + (8 \times 1s.\ 9d.)}{8} = £15.$$

In the latter part of 1859 the miners received 90*l.* per ton of copper in the ore, when the selling price of copper was 112*l.* 10*s.* Hence, in smelting at that time there should have been 7*l.* 10*s.* profit on smelting per ton of copper. But this would not represent the *actual profit* of the smelter, as certain commercial expenses, such as discount, &c., connected with the sale of the metal, would have to be deducted.

According to one smelter the cost of reduction at large works with which he was connected was 1*l.* 3*s.* 4*d.* per ton of ore on the average; and the cost on the ton of copper never exceeded 10*l.*, but was often less.

Cost of copper-works and capital required.—The cost will obviously vary considerably with the locality and nature of the site; it may be necessary to construct expensive wharves or quays, and in every case a large piece of spare land is required on which to deposit slags, ashes, and other waste. I am informed that works on the *smallest* scale to afford any prospect of success should be capable of making 1100 tons of fine copper per annum from a good mixture of ores yielding, say on

[3] Procédés Métall., p. 414.

an average, 10 per cent. Such works would contain about 18 furnaces (say 6 calciners and 12 others) with all the necessary accompaniments, and may be estimated at a cost of 9500*l*. or 10,000*l*. The calciners may be estimated at 240*l*. and the melting furnaces at 200*l*. each, exclusive of workmen's tools, &c. The additional capital needed to carry on the concern in an independent manner should be 35,000*l*., making a total of 45,000*l*. If such works were judiciously constructed with a view to future extension, their capacity might be doubled at an outlay of about 50 per cent. of the original cost.

Fuel is the largest item of expenditure in copper-works, and consequently a situation where suitable and cheap coal can be obtained is of great importance. The quantity of coal consumed will vary much with its quality, and in a greater or less degree with the nature of the ores and the economy of management; but it may be generally estimated that in works such as those supposed there would be an annual consumption of about 20,000 tons of coal, or for every ton of copper made from a mixture of ores yielding 10 per cent. of copper, 18 tons of coal.

The cost of smelting will vary materially with the rate of wages, prices of iron, bricks, and other articles which are largely consumed in copper-works. It may, however, be estimated that in producing 1100 tons of fine copper in such works and from such ores as those above supposed, there will be an expenditure of 9600*l*., or about 8*l*. 15*s*. per ton of copper produced. This is the cost of smelting only, exclusive of interest on capital, carriage of ores from mines to port, freight from ports to smelting works, cost of carrying copper to market, expenses attending purchase of ore and sale of copper, with other incidental charges, which vary according to circumstances, such as position of works with respect to supply of ore, proximity to markets, &c.

The profit in copper-smelting must depend in great measure on the possession of ample capital and the exercise of sound commercial judgment in the purchase of ores and the sale of copper. A series of advances in the price of copper may treble the ordinary profits of the smelter; and, on the other hand, a series of falls in the price may not only absorb the profits, but occasion loss. The price of copper is liable to oscillations so considerable and sometimes so unexpected as to render mercantile operations connected with the metal not a little uncertain.

The mistake is sometimes made of confounding the management of smelting works with the management of the mercantile business connected therewith—departments which are essentially distinct from each other. It is one thing to know how to *make* iron or copper, and it is another thing to know how to *sell* the metals. The possessors of mineral property would do well to bear this in mind. The proprietor of estates containing valuable measures of coal and ironstone, seeing the prosperity of a neighbouring ironmaster who pays heavily for a lease of both, might be led to conclude that he ought certainly to rival, if not excel, this neighbour in prosperity by smelting his own ores with his own fuel; and he may make the experiment and discover that he has

been egregiously mistaken in his calculation. He may have succeeded in the metallurgical, but have signally failed in the mercantile part of the business.

Turning over of capital.—Capital cannot be turned over in copper-smelting more than 2½ times a year when trade is *good*, and 2¼ times is a fair average. It is questionable whether any concern on an average of 10 years makes 13 per cent. on capital, inclusive of interest at 5 per cent. per annum. In exemplification of the fluctuating state of the copper trade, I may introduce the following facts, which I have received on authority, namely, during two years, about 1839, one of the largest and best conducted firms in Swansea did not realize more than 5 per cent. per annum; and in 1860 another of the principal firms in Swansea actually lost money.

Profit of copper-smelters in the last century.—I am able to present some trustworthy financial information concerning copper-smelting in the last century which is not without interest at the present day. I am indebted to Mr. William Edmond for copies of balance-sheets of the Languvelach (sic) Copper-Works for the years 1743 and 1745. The capital was 20,000*l.* in 40 shares divided amongst seven proprietors—R. and Jno. Lockwood, R. Morris, Edw. Elliston, &c. From December, 1742, to December, 1743, the profit amounted to 4382*l.* 0*s.* 10*d.*; and from December, 1744, to December, 1745, it only amounted to 945*l.* 5*s.* 9*d.*

Through Mr. Francis, of Swansea, I have had access to private journals which appear to have been written during the latter part of the last century by "J. Morris, Forest Copper-Works," as this name and address are recorded at the beginning according to the usual practice. In January, 1775, is the following entry: Rough sketch of profits—Copper-Works about 8000*l.*; Mills 1000*l.*; Plas y Marl 1276*l.* It was estimated that in order to smelt in one year 4732 tons of ore, supposed to contain on an average 2 cwt. of copper, and expected to yield 473 tons 4 cwt. of *fine copper*, 11 calciners, 21 smelting-furnaces, and 2 refineries would be required; and it was recommended that there should be an additional calciner to be used in the event of one of the others requiring repairs. The weekly consumption of coal was estimated as follows:—

	Weys.	Loads.
21 smelting-furnaces	27	..
2 refineries	2	8
11 calciners	8	40
	37	48

A wey is about 10 tons. This estimate is signed by Martin Bevan, and it is stated to refer to the old method of smelting, in which *the metal* (regulus) *was ground.*

In Mr. Morris's journals are estimates, which I subjoin, of the expenses of building three different sorts of calcining-furnaces at the Forest Copper-Works, Jan., 1786, and which are interesting as showing the price of materials, labour, &c., at that period.

	1.		2.		3.	
	Tons.	£. s. d.	Tons.	£. s. d.	Tons.	£. s. d.
Stones, quarrying, carrying, barging, &c.	16 at 3s.	2 8 0	10 at 3s.	1 10 0	10 at 3s.	1 10 0
Dressing do.	32 yds. at 1s. 9d.	2 16 0	20 yds.	1 15 0	20 yds.	1 15 0
Bridgewater brick	2½ in. at 25s.	3 2 6	2 in.	1 10 0	1 in.	1 5 0
Flintshire brick	8 in. at 70s.	28 0 0	8 in.	28 0 0	7 in.	24 10 0
	Tons. cwts.		Tons. cwts.		Tons. cwts.	
Cast-iron	1 5 at £11	13 15 0	1 0	11 0 0	0 15	8 5 0
Wrought-iron	1 15 at £19	33 5 0	1 5	23 15 0	1 0	19 0 0
Mason-work and tending		15 0 0	..	12 0 0	..	10 0 0
Lime	60 bushels.	1 10 0	..	1 10 0	..	1 10 0
	£. s. d.					
Chimney, 3 in. Bridgewater brick	3 15 0					
1 in. Flintshire do.	3 10 0					
Iron, 5 cwt.	4 15 0	15 0 0	..	15 0 0	..	15 0 0
Mason-work, lime, and tending	3 0 0					
	£	117 8 6	£	98 12 0	£	85 7 0

I give the addition under each column as it is in the original. A sum of 2*l.* 12*s.* 6*d.* has been added to each of the totals; but for what reason I do not know.

I should wish it to be distinctly understood that I simply present the foregoing statements respecting smelting costs as I received them, and that *personally I cannot in any degree be responsible for their accuracy.* I am in possession of information on this subject which I cannot in honour reveal; but I may state my impression that in the present day a copper-smelter has not much chance of adding to his wealth, if he is not a shrewd, judicious, and energetic man of business.

COST OF COPPER-SMELTING AT ÅTVIDABERG IN PRODUCING 1 SWEDISH CENTNER OF REFINED (GAAR) COPPER.

Materials employed in making 1 centner of refined copper.	Centners.			Rix-dollars (Mynt).	Rix-dollars (Mynt).
Ore	15·27	Wages in raising and carrying ore	at 0·66 per centner		10·08
		Calcining			0·21
Residua, slags, &c.	6·23	Do. remelting	at 0·10	do.	0·62
Regulus	5·23	Do. crushing, carrying	at 0·265	do.	1·39
Black copper	1·17	Smelting, refining, and regulus-calcining			0·83
Coke, total	3·48		at 1·86	do.	6·36
Charcoal, total, for smelting and refining	6·87		at 0·80	do.	5·50
	cub. feet.				
Wood, in calcining ores	6 77		at 0·04 per cub. foot.		0·27
Do. in calcining regulus	7·92		at 0·04	do.	0·32
			Rix-dollars (Mynt)		25·58
					£1 8 5

18 Rix-dollar (Mynt) = £1
1 do. do. = 13·33*d.*
1 Swedish centner = 0·837 English cwt. of 112 lbs.
1 Eng. cwt. of refined copper will cost £1 13*s.* 11½*d.* very nearly, say £1 14*s.*
1 ton will cost £34. M. Malmqvist estimates it at about £40 per ton.

The total cost of making copper at Atvidaberg, per Swedish centner, including expenses of management, sick-fund, poor-rates, taxes, &c., is 42·16 Rix-dollars (Mynt), or £55 19*s.* per ton of 2240 lbs.

TABLE OF THE COMPOSITION OF COMMERCIAL COPPER FROM VARIOUS LOCALITIES.

	1.	2.	3.	4.	5.	6.	7.	8.	9.	10.	11.
Copper	99·55	99·16	99·460	98·65	99·62	98·25	98·97	96·54	99·12	98·73	...
Dioxide of copper	...	...	...	...	...	...	...	1·41	...	...	...
Sulphur	0·11	...	0·017	...	...	...	traces	...	...	...	...
Iron	0·15	0·05	0·011	0·05	0·02	0·13	0·23	0·78	0·17	0·07	0·03
Lead	0·19	0·48	scarcely a trace	0·75	traces	1·09	0·07	...	...	0·74	...
Tin	...	...	Ditto	...	0·27	...	...	...	...	...	minute traces
Silver	...	0·23	0·065	0·22	traces	0·13	0·13	...	...	0·06	...
Gold	...	...	0·0015	...	...	...	...	...	...	...	minute traces
Nickel	...	...	0·110	...	...	0·24	0·27	...	...	trace	0·13
Cobalt	...	...		...	...	...	...	...	...	0·14	...
Manganese	...	0·05	...	...	traces	...	...	...	...	...	...
Potassium	...	...	...	...	...	...	0·07	...	0·38	0·17	...
Calcium	...	...	...	0·09	...	0·11	0·04	...	0·33	0·09	...
Magnesium	...	...	...	0·03	...		traces	...	...	...	...
Aluminium	...	...	...	0·02	0·09	0·05	...	...	...	...	...
Vanadium	...	...	...	...	...	...	...	0·21	...	...	...
Silicon	...	...	...	0·05	...	...	...	...	...	...	...
Slag	...	0·03	...	...	...	...	0·22	...	...	...	...
	100·00	100·00	99·6645	99·86	100·00	100·00	100·00	98·94	100·00	100·00	...

1. Refined copper from Gustavsberg and Carlsberg, Sweden, by Genth. 2. Refined copper from Avesta, Sweden, by Genth. 3. Refined copper from Åtvidaberg, Sweden; analysis made at the Mining School, Fahlun. 4. Swedish Rosette copper; locality not given, by Von Kobell. 5. Norwegian copper, by Genth. 6. Rosette copper from Mansfeld, by Von Kobell. 7. Refined copper from Riechelsdorf, by Genth. 8. From Perm, Oural, by Choubine. 9. A variety of copper imported from Switzerland into France, said to be remarkable for its softness and flexibility, by Berthier. 10. Japanese copper, by Genth. 11. Specimen of Japanese copper brought by H.M. Consul in China, Harry Parkes, by A. Dick.

It is somewhat remarkable that no mention of antimony or arsenic is made in any of the foregoing analyses; and yet, probably, no metals are more frequently present in commercial varieties of copper. A curious fact may here be stated concerning the occurrence of arsenic in copper of extremely ancient date. A flat piece of copper, supposed to have formed the blade of a knife, was discovered in boring a few years ago, at a depth, it is alleged, of 13 feet from the surface, below the site of the statue of Rameses the Second, who is believed to have reigned in Egypt about 1400 B.C. A portion of the copper was analysed in my laboratory, at the request of Mr. Leonard Horner, by Mr. C. Tookey, and found to be composed as follows:—

Copper	97·12
Arsenic	2·29
Iron	0·43
Tin with traces of gold	0·24
	100·08

The effect of the arsenic would be to communicate hardness; but this blade, which contained 2¼ per cent. of arsenic, was, nevertheless, so soft that it could not have been an effective cutting implement. The presence of arsenic in this ancient relic may possibly have been accidental. The late Mr. Henry and myself detected antimony in a specimen of copper which I received from the late Mr. Paul Moore, a large consumer of copper in Birmingham, and which was reputed to have been made exclusively from the fine Burra-Burra ores. In a specimen of copper recently examined in the Metallurgical Laboratory about 30 oz. of antimony to the ton were found: when rolled plates of this copper were cut with shears, the edges had a peculiar roughness. Bismuth does not appear in these analyses, and yet it is occasionally present in very sensible quantity. Iron is generally present in copper; and, although the proportion is usually very small, yet it should be borne in mind that a considerable amount of this metal may be retained by copper. A singular copper-like ancient coin from India was submitted to me for analysis by my friend Mr. Edward Thomas, so well known for his acquaintance with the coins of India.[4] When broken across, its fracture was finely granular. It was found by Mr. C. Tookey to consist of—

Copper	94·59
Iron	5·06
	99·65

[4] Mr. Thomas has communicated the following information respecting this coin:—"An engraving of a coin of similar types to that of which the analysis is given above, is to be found in the 'Journal of the Asiatic Society of Bengal,' vol. vii. plate xxxii. fig. 12, and in Prinsep's 'Essays' (London, 1858), pl. xliv. fig. 12. The obverse, which has been struck with an effective and well-cut die, bears the Buddhist device of a man, with the legend, in old Páli letters, *Khatrapasa Pagimashasa*. The reverse exhibits a rude figure of a horse, which, unlike the device of the obverse die, seems to have been merely sunk into the anvil as a catch to fix the planchet. This class of coin is supposed to have been issued by the local sovereigns of the Sub-Himalayan Gangetic provinces prior to the introduction of Greek art. See Prinsep's 'Essays,' vol. i. p. 222."

Copper Sheathing.

Sheet copper is largely consumed in sheathing H. M. ships of war; and extraordinary differences have been observed in the manner, in the degree, and in the rapidity with which different samples of copper are corroded by sea-water. The sheathing may be pretty uniformly corroded over the entire bottom of a ship, or it may only be sensibly attacked here and there on the surface of particular plates; it may be eaten away so as to form irregular holes, sometimes of considerable size; it may be exposed during many years to the action of sea-water without presenting any marked sign of corrosive action, or in the course only of a few months it may become so honey-combed and full of holes as to be no longer serviceable. I have inspected a large number of specimens of copper sheathing which have been stripped off the bottoms of H. M. ships from time to time, and the results of my observation are such as I have just recorded.

When copper is exposed to the action of sea-water, its surface acquires a green coating, which chiefly, I believe, consists of oxy-chloride of copper, formed by the conjoint action of the chlorides in the water and atmospheric air. When this coating has once formed, complex local electrical actions probably occur, and may occasion the formation of compounds either new or as yet very imperfectly understood. During many years I have had experiments in progress on such local actions, and the results are not a little complicated and perplexing. I had the opportunity in Paris some years ago of inspecting a piece of old copper sheathing on which were small but distinct crystals of dioxide of copper. A thorough investigation of the composition of the products of corrosive action would be extremely instructive. It is possible that researches of this nature have been made and published; but, if so, I have not been so fortunate as to meet with the record of them.

It has, I believe, been satisfactorily established that in some localities corrosion proceeds more rapidly than in others; and this has been attributed to differences in the quality of the water. Thus, the late Professor Daniell of King's College investigated the question of the rapid destruction of copper sheathing on the African station, and arrived at the conclusion that it was due to the presence of sulphuretted hydrogen in the water.[5] To the same agent his successor, Dr. Miller, has recently referred the rapid corrosion of yellow-metal (see the article on Brass) which is alleged to occur in the London Docks. The copper-smelters and others who manufacture this metal were so impressed with the belief of the extremely corrosive nature of the water of these docks, that some time ago they jointly agreed to refuse their usual guarantee for the durability of the metal during a

[5] It is recorded (p. 57) in the Report of the Committee appointed to enquire into the state of the Copper Mines and Copper Trade of the Kingdom (ordered to be printed May 7, 1799), that a Liverpool merchant-vessel was sheathed with copper in April, 1785, had made *sixteen* voyages from Liverpool to the coast of Africa, thence to the West Indies and back to Liverpool, and, after insignificant repairs, the copper in April, 1799, was still *good*.

certain term, in the case of vessels entering and lying in the London Docks. They were supported in this step especially by the evidence of Dr. Miller, who declared that the dock water was strongly impregnated with sulphuretted hydrogen, and was therefore likely to act injuriously upon the metal by the formation of metallic sulphides on its surface. But the Company, it should be stated, established conclusively that the yellow metal sheathing now in use varies remarkably in the degree of rapidity with which it suffers corrosion.

Now whatever truth there may be in the statements as to the greater corrosive action of sea-water in particular localities, it has been established, on unquestionable evidence, that commercial copper differs remarkably in its power of resisting that action. Very numerous observations and comparative experiments on this point have been made in H.M. dockyards, and from the results which have been recorded I insert the following by way of illustration:[6]—

Oct. 5, 1845, the "Vanguard" was sheathed on the starboard side with 400 sheets of copper (C) smelted and manufactured exclusively from Cornish ores by Messrs. Grenfell and Co., and at the same time the port side was sheathed with 400 sheets of copper (F) made from a mixture of British and foreign ores. May 29, 1849, 19 sheets were taken off from each side and weighed, these sheets having been previously separately weighed and marked for the purpose of identification. The original weights of the sheets (C) ranged from 7 lbs. 8 oz. to 9 lbs. 8 oz., and the original sheets (F) ranged from 8 lbs. 6 oz. to 9 lbs. 15 oz. The results are given underneath:—

	Average Loss per Sheet.	Average Loss per Sheet per Annum.
C	9·32 oz.	2·66 oz.
F	15·32	4·38

The "Sappho" was wholly sheathed with copper "of Chatham manufacture, 1847" (C)—by which, I presume, is meant copper from various sources remelted, cast, and rolled at Chatham—with the exception of 50 sheets, on each side, of copper smelted at Swansea by Messrs. Williams, Foster, and Co. (H). This copper is designated in the Reports as "hard metal sheathing," and its use was suggested by Mr. Moyle, an experienced practical smelter formerly in the employ of the firm above-mentioned, but now engaged at Chatham Dockyard. This "hard copper" is described as having been "separated from the soft at a certain process of smelting," from which it may be inferred that it consisted of the "bottoms" reduced in the process of making *best selected*. Of this "hard copper" 30 tons were refined under Mr. Owen's inspection at Swansea in 1846, and in the refining much less lead was added than usual. The refined "hard copper" was rolled into sheets and employed in several experiments. A portion was submitted to Mr. Pridcaux, who states that he found it to contain the following foreign matters:—

[6] When no particular authority is given for statements in the following pages, it must be understood that they have been derived from official documents.

	Per cent.	
Zinc	0·200	
Iron	0·076	
Nickel	0·040	
Tin	0·019	
Lead	0·007	0·491
Silver	0·001	
Antimony	0·024	
Arsenic	0·124	
Manganese	traces	
Silicon	0·035	
Aluminium	0·010	
Calcium	0·055	0·154
Magnesium	0·007	
Potassium and sodium	0·047	
		0·645

Mr. Prideaux remarks that the silicon and following ingredients "may have possibly been dissolved from the glass in which the copper was boiled with acid." This possible source of error did not probably occur to Mr. Prideaux until he had completed this most elaborate analysis, for otherwise he would hardly have expended the time necessary to determine these ingredients quantitatively.

The "Sappho," thus coppered, had been lying in Portsmouth harbour only 12 months, when her sheathing was found to be so much deteriorated, being in some places eaten away in holes, that it was necessary to remove not fewer than 80 sheets. The average loss per sheet of C was 16¾ oz., while the average loss of H was only 2¾ oz.

It is recorded that some of the same "hard metal" sheathing was tried on a merchant ship, the "Esk," belonging to Mr. Brocklebank, and reported on most favourably.

In the case of H.M. ship "Howe" at Sheerness in 1847, there were two different kinds of copper on her bottom: one the old copper manufactured at the Portsmouth Metal-Mills, and the other new cake-copper produced from a mixture of British and foreign ores, and supplied by contractors. With the former (probably manufactured in about 1832-1833) the average loss per sheet per annum was only 0·79 oz., or 11 oz. in 14 years; whereas with the latter (smelted and manufactured in 1843) the average loss per sheet per annum was 4·3 oz., or 15 oz. in 3½ years.

I find it recorded that copper sheathing was first applied in the Navy in 1761, when one ship was coppered; a second was coppered in 1765, a third in 1770, four in 1776, nine in 1777, and within three years from the last date all the ships of the British Navy were coppered.

It is maintained that the copper formerly employed in the Navy resisted the corrosive action of sea-water much better than that produced in recent times, and that manifest deterioration in the quality of copper sheathing commenced about 1832 or 1833. From the peace in 1815 to 1832 no copper had been purchased for the Navy, a sufficient supply of new sheathing having been obtained during this period by re-melting

and re-manufacturing the old sheathing. Now it is stated that the smelting of foreign in admixture with British copper-ores was introduced during the years 1833, 1834, and 1835; and hence the commencement of deterioration in the quality of the copper is found to be nearly coincident with the introduction of foreign copper-ores into this country, or at least with the introduction of new copper into the Navy. The following table, extracted from official records, may be interesting to copper-smelters:—

TABLE SHOWING THE AMOUNT OF CORROSION IN SHEATHING MADE FROM DIFFERENT KINDS OF COPPER, FROM 1816 TO 1844 INCLUSIVE. The copper was examined or taken off between July, 1843, and Dec. 1845.

Name of the Ship.	Station.	Date of Manufacture of the Sheathing.	Average Loss per Sheet per Annum.
			oz.
Armada	Hamoaze	1816	0·83
Fountain (water-tank)	Plymouth Sound	1817	0·55
Chatham (breakwater vessel)	do. do.	1817	0·33
Semiramis	Sea and harbour	1821	0·82
Nereus	Hamoaze	1821	0·85
Netly (tender)	Sea and harbour	1823	0·66
Armada	Hamoaze	1824	0·75
Chatham	Plymouth Sound	1825	0·57
Impregnable	Sea and harbour	1825	0·66
Netly (tender)	do. do.	1826	0·75
Beresford (hoy)	Plymouth	1828	1·25
Stag	Hamoaze	1829	1·50
Cyclops (S. V.)	Sea	1829	1·75
Light vessel	Breakwater	1832	0·50
America	Hamoaze	1832	2·25
Forth	do.	1833	1·00
Grecian	Sea	1835	6·13
Falmouth (lighter)	Sea and harbour	1837	1·25
Cyclops (S. V.)	Sea	1838	3·20
Nimrod	do.	1838	5 20
Forth	Hamoaze	1838-9	11·00
Endymion	Sea	1840	5·33
Calcutta	do.	1840	4·50
Vanguard	do.	1840	0·90
Indus	do.	1840	4·50
Clarence	Hamoaze	1840	2·66
Volage	Sea	1841	7·33
Superb	Hamoaze	1842	1·33
Royal William	do.	1842	2·56
Pandora	do.	1843	11·33
Melampus	Sea	1843	6·00
Do.	do.	1844	6·00
Persian	Hamoaze	1844	4·17
Acorn	do.	1844	6·50
Daring	Sea	1844	1·00

It appears from this table that the transition from good to bad copper was abrupt, and occurred about 1833, as previously stated.

But notwithstanding the conclusion to which the results in the foregoing table would lead, it is certain that all the old copper was not good, and that all the new copper is not bad.

In support of the first proposition the following evidence may be

adduced. Mr. Owen had access to the papers of Sir Samuel Bentham, and extracted from them this tabular record:—

Ship's Name.	When taken off.	Duration of Sheathing.		Remarks.
		Years.	Months.	
Repulse.....	Dec. 1808.....	2	6	Copper in state of corrosion.
Dragon	Feb. 1807.....	2	4	Worn thin.
Encounter	Jan. 1808.....	2	8	Do.
Melpomene	Jan. 1808.....	2	5	Copper corroded.
Dryad	June, 1808.....	2	11	Do. and very thin.
Lark	Sept. 1808.....	3	0	Do. worn thin.

EXTRACTS FROM DOCKYARD REPORTS.

Portsmouth Yard.—"H.M. ship 'Intrepid,' stripped in Dec. 1796. The copper was of the most approved sort, but it was only on 4 years. Copper fastened; $\frac{1}{3}$ of the copper was much corroded, very foul, and in general very bad."

Sheerness Yard.—Report of the officers to the Navy Board, March 9, 1797:—

Ship's Name.	Marks on the Sheet.	How long on.	Loss per Sheet per Annum.	Observations.
		Years.	oz.	
Adamant	28 oz. $\frac{R}{C}$ &c. ...	8	1·56	Good.
Hind	28 oz.; no mark	10	1·85	Do.
Ariadne.....	28 oz.	$4\frac{1}{2}$	3·22	Middling.
Do.	32 oz.	$4\frac{1}{2}$	13·65	Bad.
Proserpine	28 oz. $\frac{PM}{C}$	6	1·56	Good.
Latona	28 oz. $\frac{R}{C}$ &c. ...	7	1·21	Do.

Plymouth Yard, Feb. 22, 1797.—"The officers send to the Navy Board a sheet from the 'Chatham,' and supposed to have been on 18 years; not the least appearance of corrosion or foulness, like the *Copper now in use* [sic in ital.], except on the nails, which being of mixed metal are very foul with barnacles and long weeds hanging to them. They also send a sheet taken from the bottom of H.M.S. 'Sheerness,' of the improved sort of copper, on little more than 3 years, marked 'Owen Williams,' and eaten through in many places, but not so bad as those taken from the same ship and returned to the contractor. From these circumstances, they say, together with many general observations we have had it in our power to make, we are fully convinced that the copper now in use (1797) *is adulterated*, and that to a very great degree."

"The master shipwright recollects the 'Dædalus' being coppered by him at Liverpool in 1780, and also its being taken off again under him in the river Thames in 1791, a period of 11 years, when it was found to be in a very perfect state without any corrosion, and a square foot of the 32-oz. copper not to have lost in weight more than

3 or 4 oz., and that evidently from wear; whilst he recollects many other instances of copper not having been on more than 2 years, and its being eaten quite through. This, with what here passed under our own notice at this yard, confirms us in our opinion of its being greatly adulterated."

The then Navy Board were so impressed with the deterioration in the quality of the copper used for sheathing, which appeared to have commenced about the year 1786, that they employed Dr. Higgins, of Greek Street, Soho, to make analyses of the copper with a view to ascertain how far the presence of foreign matters might influence the corrosive action.

Dr. Higgins reported that he found the copper to be alloyed with about 2½ per cent. of lead, and other metals (chiefly tin and antimony) in much smaller quantity; that copper so alloyed is apt to be injured in repeated annealing, especially when coal is used as fuel, and is more easily penetrated and corroded by the salts contained in sea-water.

In support of the other proposition, that all recent copper-sheathing is not bad, the following experimental results may be cited:—

In October, 1845, the "Superb" was sheathed on the starboard side with 400 sheets of copper produced exclusively from Cornish ores by Messrs. Grenfell and Co. (G), and on the port side with the same number of sheets of old re-manufactured copper rolled at Portsmouth (P). On Feb. 24, 1849, it was reported from Portsmouth Dockyard that both kinds of copper on this ship were found on examination to be remarkably free from corrosion, and less foul than has usually been observed in copper on the bottoms of ships after having been so long afloat. The actual results are as under:—

	Average Loss per Sheet per Annum.
G	2·34 oz.
P	2·12

Great differences were noted in the degree of corrosion in a few of the plates, especially in the case of G: thus one plate, which originally weighed 8 lbs. 10 oz., lost 17 oz.; whilst two other plates, which originally weighed 9 lbs. 3 oz. and 9 lbs., are stated to have lost nothing in weight; in the case of P the extremes were losses of 3 oz. and 10 oz. in plates which originally weighed 9 lbs. 3 oz. and 8 lbs. 3 oz. respectively. It is suggested that the great loss in some of the plates of the most corroded (G) might have been caused by bad rolling.

There are many persons, both in and out of the House of Commons, who stoutly maintain that in no case is it desirable that the Government should engage in manufacturing operations, and that it would better consult the interests of the nation by contracting with private manufacturers for any work which may be required to be done; and grave charges of reckless expenditure and general maladministration in H.M. dockyards have recently been brought against the Admiralty by members of Parliament, eminent engineers, shipbuilders, and others. While it is admitted that in some instances these charges are well founded, yet, in common justice, it deserves to be recorded that the Government has acted wisely in not always trusting too implicitly in

matters of business to the disinterested patriotism of our manufacturers. In proof of this the following somewhat startling facts may be adduced :—

The attention of Sir S. Bentham was directed, in 1803, to the large expense incurred by the Navy in the re-manufacture of old copper-sheathing. At that time the re-manufacture of this old metal was conducted by private manufacturers, who were paid at the rate of 4½*d.* per lb., or 42*l.* per ton. At the recommendation of Sir Samuel, metal-mills were erected at Portsmouth expressly for carrying on this work, when the private manufacturers offered to reduce their charges to 2½*d.* per lb.; but it was effected at the Portsmouth Mills at a cost only of 1½*d.* per lb. Subsequently, in 1833, Mr. Owen prepared an account in obedience to a precept of the House of Commons, and showed that the cost of re-manufacturing old copper was—

For sheathing	0·86*d.* per lb. or	£8	0*s.* 10½*d.* per ton.
And for bolt-staves	0·65*d.* ,,	£6	0*s.* 10½*d.* ,,

It was calculated that, at the period above-mentioned, the saving to the nation, by the adoption of Sir S. Bentham's recommendation, must have amounted to some hundreds of thousands of pounds; so that the private firms, who had previously done the simple work of re-melting and rolling the old metal, must have had what in common phraseology are termed *capital pickings* out of the national purse.[7]

The re-melting of the old copper was effected in reverberatory furnaces, and was attended with the formation of a considerable quantity of slag containing, like *refinery-slag*, a large amount of copper; and until a few years ago this valuable product was usually, if not always, consigned to the *dust-heap!* Not only was there rich copper-slag produced in the re-melting of the old metal, but also in the *re*-refining of new copper, which was formerly done.[8] It is scarcely credible that the persons entrusted with the direction of the furnaces should have been so grossly ignorant of the metallurgy of copper as to have permitted this waste; and yet such is the fact, which I should not venture to publish if I were not in possession of indisputable evidence of its truth. It is not possible to estimate the loss which the nation must thus have sustained through sheer ignorance. There are probably accumulations of copper-slags in some of H. M. dock-yards or the vicinity which present a more promising field for mining enterprise than many a *sett* in Cornwall or Devon. It may, unfortunately, be found on inquiry that these rich cupriferous deposits now lie at inaccessible depths, or have been washed away. At all events the subject is worthy of consideration from mine-adventurers, who are not averse to a plausible

[7] It is stated that the officials in estimating the cost of manufacture in Government works do not, like private manufacturers, include interest on plant and certain other items of necessary expenditure. I do not know whether the sum stated above was thus deduced; but if so, the alleged saving to the nation must have been less than the amount given.

[8] I find a note to the effect that Messrs. Vivian and Co. called the attention of the officials to the very unnecessary expense incurred in repeating the process of refining without any corresponding advantage.

speculation; and Chatham Dockyard might be chosen as the scene of the first exploration.

It must not be supposed that blunders such as that which we have just been considering could only occur in Government establishments; for, that they may be perpetrated in private establishments is proved by the fact, that some years ago it was the practice at tin-plate works to throw away a black dust containing much more than half its weight of tin! In conjunction with the late Mr. Henry I visited tin-plate works in South Wales, and procured specimens of this dust, in which Mr. Henry found 60 per cent. of tin, and which, we were told by the manager, had in former years been thrown into the river hard by.

Notwithstanding the Lords of the Admiralty have during the last sixty years directed their assiduous attention to the subject of the corrosion of copper sheathing—notwithstanding the reports of committees on metals—the laborious investigations of supervisors of metals—the vast accumulation of recorded observations—the innumerable experiments made in H. M. dockyards—the information obtained through the Foreign Office from other governments—the analyses of Mr. Prideaux and others—it must be confessed that we have obtained but very little positive knowledge as to the causes of what may be termed the *corrosive susceptibility* of different qualities of copper. That the investigation of these causes is one of great difficulty there can be no doubt; but I firmly believe that the difficulty is far from insuperable; and my impression is that a solution of the question is not likely to be arrived at through the complex machinery and divided responsibility of committees.

The question, it appears to me, should be specially considered under two distinct heads, namely, the physical state of the metal employed as sheathing, and the chemical composition of the copper from which it is prepared.

In a former part of this volume it has been shown that copper cast under ordinary conditions, and which externally appears perfectly sound, yet contains innumerable pores or minute more or less spherical cavities diffused through the mass. Now, by no process of rolling is it conceivable that *absolutely solid* copper should be produced from that abounding in such cavities, though, after rolling, they may cease to be visible even by the aid of a microscope; and, if this be admitted, the structure of the metal will not be perfectly uniform through the mass, or over the surface of a rolled sheet. But want of uniformity of structure would lead us to anticipate corresponding differences in the degree of action of corrosive liquids upon the surface of the metal, especially such as operate slowly, like sea-water. The only specimen of cast copper which I have ever seen apparently quite free from diffused cavities is that which was melted under charcoal and poured through an atmosphere of coal-gas; and it would be desirable to institute experiments with sheathing rolled from copper cast in this manner. The porosity of the copper-rolls employed in calico-printing has been a frequent subject of complaint, and various expedients have been resorted to by copper-smelters to obviate the defect, but hitherto,

I believe, with only partial success. In casting these rolls it is now a common practice to pour the melted metal into strong cylindrical moulds of iron, and immediately afterwards to subject it to great pressure by means of levers acting upon an iron piston, which is introduced at the top of the mould above the surface of the copper: the copper is thus allowed to solidify under constant pressure.

An experiment was made on the "Rodney" to ascertain whether copper hardened by rolling was less subject to corrosion than the same copper in its usual soft state. On the starboard side 23 sheets of hard rolled copper were fastened, and on the port side 23 sheets of the same copper in the soft state in which it is usually employed. After five years no perceptible difference was observed in the degree of corrosion in these two kinds of plates.

With regard to the determination of the composition of the copper employed as sheathing, it cannot be expected that any results of much practical value will be obtained except by very expert chemical analysts. The detection, and quantitative determination especially, of foreign metals or other matters, when present only in minute quantities in a metallic mass, are often attended with extreme difficulty; and in many cases the known methods of analysis will not yield correct results. In a proper investigation of the exact composition of various descriptions of copper, it would be absolutely necessary to search for new methods or attempt to improve old ones, in order to enable the operator to arrive at satisfactory results; and this would require considerable time and persevering labour both of head and hands. The Lords of the Admiralty, having no experience of the slow and tedious nature of analytical manipulations, may, like many other persons equally unacquainted with the subject, be disposed to imagine that a chemist should be able to present them with a correct analysis of a piece of copper with as much facility and with almost as much rapidity as a physician can write a prescription. In order to ascertain the causes of the different degrees of corrosion observed in different qualities of copper, in so far as they may be connected with chemical composition, it would be necessary to expend a considerable sum, and to wait patiently for the analytical results.

When the corrosive action takes place very irregularly over the same sheet of copper, the cause will probably be found to depend on corresponding irregularities in the diffusion of foreign matter; and it is not unlikely that lead may play a frequent part in determining local action; for this metal, it will be remembered, is always put into the refining furnace before lading for *cake*-copper—or that from which copper sheathing is rolled—and a very sensible quantity of it remains permanently in the copper. But lead mixes, rather than alloys, with copper, and is therefore apt to be disseminated irregularly through the mass of the copper. Since the introduction of foreign ores, which are frequently contaminated with antimony, it has, I believe, often been found necessary to use an additional dose of lead in refining. We have seen that there is reason for believing that *cake-copper* always contains dioxide of copper; and as this may be irregu-

larly diffused through, rather than dissolved in, the metal, it may possibly prove to be one cause of local action. There is some ground, I think, for supposing that the presence of a little tin may tend to render copper less liable to corrosion by sea-water. The Agordo copper, which contains tin, is said to be in much request for ship-sheathing. A patent was granted in 1830 for the application of copper alloyed with from 4 to 6½ per cent. of tin to the sheathing of ships; and it is stated in the specification that lead and zinc, in very small proportions, might be mixed therewith.[9] I understand that sheathing made of this alloy was actually manufactured at Swansea, but that it was difficult and expensive to roll on account of its hardness. I have not been able to ascertain whether it was ever satisfactorily tested at sea.

We have seen how remarkably the structure of an ingot of copper is modified by the presence of various and chemically dissimilar foreign matters; and I should counsel the Admiralty, if they persevere in the use of copper, in preference to yellow metal, sheathing in the Navy, to have a series of experiments conducted by thoroughly trained and competent persons, to determine, with respect to the action of sea-water, the preservative effects or otherwise of various metals and other elements upon copper.

When the British Association met at Swansea in 1848, I had the honour of delivering a lecture to the members explanatory of the metallurgical operations practised in the town and its vicinity. I prepared in Birmingham, where I then resided, various specimens to illustrate the effects of certain foreign matters upon copper, such as sulphur, phosphorus, &c. My friend Colonel Sir Henry (then Captain) James, R.E., Director of the Ordnance Survey of Great Britain, saw these illustrations, and, at that time holding an appointment in Portsmouth Dockyard, expressed a wish to ascertain the relative action of sea-water upon them. With that wish I readily complied, and furnished Sir Henry with portions of three specimens. He proceeded to experiment upon them during nine months; and the results were communicated to the British Association at Birmingham in the following year (1849), and were subsequently published in extenso in the 'Chemical Gazette.'[1] I now republish them, as they may not otherwise be accessible to persons interested in this important subject. (*See* Table, p. 515.)

Nos. 1, 2, 3, were the specimens supplied by myself. Sir H. James states that the surface of No. 3 was perfectly smooth, and tarnished with a green tint which would delight an antiquarian. The proportion of arsenic in No. 2 was not ascertained, though its presence was clearly detected: the metal was prepared by dropping metallic arsenic into melted copper.

The protective influence of phosphorus appeared so decided and remarkable that Sir Henry James applied to the Admiralty for permission to test the effect of phosphorus upon copper on a sufficiently large scale and under conditions calculated to afford decisive results.

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[9] To Matthew Uzielli, A.D. 1830. No. 5952.

[1] 1850. 8. p. 1.

TABLE OF SIR H. JAMES'S RESULTS.

No.	Quality of Metal.	Original Weight.	Weight after 9 Months.	Actual Loss.	Area of Specimens.	Loss per Square Inch.
		Grains.	Grains.	Grains.	Square in.	
1	Electrotype, rolled but not melted	348	344½	3½	2½	1·4
2	Copper, containing arsenic...	323	320	3	2½	1·2
3	Copper, containing phosphorus and iron, of which the analysis is given at p. 280.	222	222	0	2½	0·0
4	Copper, from H.M. ship "Frolic," eaten into holes in a few months, re-melted and rolled out thin.....	97	80	17	15	1·12
5	Dockyard copper	157	152	5	3	1·66
6	Do. do. another specimen	262	253	9	3	3·0
7	Do. do. do.	251½	245	6½	2·625	2·48
8	Do. do. do.	597	590	7	3	2·33
9	Muntz's metal	213	210½	2½	2·625	0·95

The permission was granted, and a sum of 50*l.* was allowed for the purpose. The phosphorized copper was prepared by Mr. J. P. Marrian of Birmingham, under my supervision. Best-selected copper was used. A portion of it was melted in a crucible, and phosphorus was gradually dropped in, a copper rod being used for stirring, in order to avoid the presence of iron. An ingot of copper was thus prepared, containing 9 per cent. of phosphorus. This phosphorized copper was then melted with the remainder of the copper in crucibles, and cast into ingots suitable for rolling. The metal, as has been previously remarked, could not be rolled at the usual temperature, but rolled well at a lower temperature, or when cold. The rolling was effected at Mr. Clifford's mill. The rolled sheet was analysed by myself, and found to contain ½ per cent. of phosphorus, the proportion it was agreed should be introduced. The sheets were duly delivered, and were placed upon buoys at three different dockyards. In a year or two afterwards Sir Henry James and myself endeavoured to ascertain the results, but in vain. We had interviews with Sir Baldwin Walker and Captain Mylne; and though nothing could be more courteous than the behaviour of these gentlemen, and though they were desirous of providing us with the fullest information as to the results, we failed to elicit more than the fact that the buoys had been painted all over! Again, after the lapse of several years, Sir Henry succeeded in ascertaining that the phosphorized sheets had resisted corrosion twice as well as others with which they had been comparatively tested.[2] It

[2] A note was furnished to Sir H. James, in which it is stated that the sheets of phosphorized copper taken from the water-line of the Stourbridge buoy lost 12¼ ozs. per sheet, whilst the loss on sheets of copper of Chatham manufacture, after exposure during the same period to the same conditions, amounted to 29¾ ozs. per sheet.

is to be regretted that further trials were not made with the phosphorized copper; for if it should be satisfactorily established by repeated experiments on a sufficiently large scale, and under varying conditions of sea-water, climate, &c., that phosphorus does diminish the corrosive action of sea-water in so decided a degree as the results above recorded indicate, it is probable that an annual saving of many thousands of pounds sterling might be effected in the Navy. It is necessary to remark that the services of Sir Henry James and myself in this matter were entirely gratuitous.

In 1857 a patent was granted to Messrs. A. and H. Parkes for the use of phosphorus as a protecting agent against corrosion in copper and other metallic sheathing.[3] Phosphorized yellow metal sheathing has, I believe, been tried on a large scale, and found not to resist better than that of the ordinary composition. I presume that after the announcement of the facts concerning phosphorized copper in 1849 to the Chemical section of the British Association in Birmingham, and their subsequent publication in the 'Chemical Gazette' in 1850, the claim of the patentees in reference to this particular metal could not be substantiated.

About fifteen years ago two samples of nails used in fastening yellow sheathing, or Muntz's metal, to ships were submitted to me for analysis; and as the results are interesting in relation to the question under consideration, I insert them underneath.

	1.		2.
Copper	62·62		52·73
Zinc	24·64		41·18
Lead	·8·69		4·72
Tin	2·64		—
	98·59		98·63

No. 1 nails were pronounced good, and appeared quite sound, after a voyage to India and back; and No. 2 nails, although apparently sound when put on, became rotten and broke off at their heads after a voyage of a few months to India. It is remarkable that those containing the largest quantity of lead resisted well; but the tin which was also present in these nails may have exerted a protective action.

According to the experience of the Dutch Navy, copper sheathing usually lasts from four to five years on sea-going ships, without requiring removal; and on ships out of or only very little in use, from ten to twelve years. It has been observed that the "purest red copper" is most liable to speedy decay, and has the appearance of being "scoured;" and that less pure or alloyed copper retains the green crust, and is more liable than the former to the adhesion of vegetable and other foreign matters. This accords with the experience of the English Navy, the green crust being found to be firm and difficult of separation in durable kinds of copper, whilst it is tender and easily scraped off those which waste quickly.

[3] A.D. 1857, Dec. 2. No. 2996.

Some years ago shipowners not unfrequently brought actions for damages against copper manufacturers on the ground that the copper sheathing supplied to particular ships had not worn so well as copper usually did or *ought* to do; and heavy damages were often awarded, though it now appears that neither the Dockyard officials nor the copper-smelters themselves have yet succeeded in preventing this uncertainty of wear, nor chemists in ascertaining the causes.

I am indebted to Mr. Thomas Wilson, of the Felling Alkali Works, Newcastle-on-Tyne, and formerly a student in our Metallurgical Laboratory, for the following description of the mode of treating on the Tyne the cupriferous residues of the pyrites imported for the manufacture of sulphuric acid (Aug. 29th, 1861). The ore used is iron-pyrites, containing about 2 per cent. of copper. The sulphur is expelled by calcination as sulphurous acid, which is conducted into sulphuric acid chambers. More sulphur generally remains in the calcined residue than is required to combine with the copper present.

1. This residue is melted in a reverberatory furnace with sand and slags from No. 3 furnace. The charge usually consists of

1 cwt. of raw ore,	3 cwt. of sand,
20 do. burnt or calcined ore,	8 do. slags.

The melting requires about 12 hours. After skimming off the slag, the *regulus* is granulated in water: it contains from 20 to 30 per cent. of copper.

2. The *granulated regulus* from No. 1 is calcined in a large reverberatory furnace having three beds. The ore is introduced at the end furthest from the grate, and is gradually pushed forwards to the hottest end. A charge of 2½ tons is put in every 8 hours; calcination lasts about 24 hours.

3. The *calcined granulated regulus* from No. 2 is melted with slags from Nos. 4 and 5: the charge consists of 34 cwt. of calcined regulus and 8 cwt. of slags. The regulus produced contains about 50 per cent. of copper, and is tapped into sand-beds.

4. The regulus from No. 3 is broken up and roasted for about 6 hours, after which it is gradually melted down and exposed to the air during about 18 hours: this process is repeated twice, in precisely the same manner, in a furnace of exactly the same construction. *Blister copper*, containing about 95 per cent. of copper, is thus produced: it is refined in the usual way.

ZINC.

HISTORY.

It is stated that Basil Valentine first employed the word zinc; but that Paracelsus, the renowned Iatro-chemist who wrote in the 16th century, was the first to associate the word with a metal possessing the distinctive characters of zinc.[1] It has, however, been admitted by Beckmann and others that this metal was first described in the 13th century by the Dominican monk Albert of Bollstedt, commonly known as Albertus Magnus. But the following passage occurs in Strabo, from which one might at first almost be disposed to conjecture that zinc in its metallic state was not unknown to the ancients:—"There is a stone near Andeira, which, being burnt, becomes iron; afterwards when melted in a furnace with a certain earth, it drops *false-silver*, which, with the addition of copper, produces what is called *the mixture*, and which some name Orichalcum.[2] False-silver is also found in the neighbourhood of Tenolus."[3] Orichalcum, or Aurichalcum, was a metallic substance so closely resembling gold in appearance, that Cicero puts the question "whether, if a person should offer a piece of *gold* to sale, thinking that he was only disposing of a piece of *orichalcum*, an honest man ought to inform him that it was really gold, or might fairly buy for a penny what was worth a thousand times as much."[4] Now, the only metallic substance which it is possible to conceive the ancients could have mistaken for gold is the alloy of copper and zinc, termed brass.

The alloy of copper and tin, termed bronze, which was well known to the ancients, could certainly never have been mistaken for gold, unless we assume that Cicero referred to a *gilded* or *plated* article; and that the gilding of bronze was practised in very ancient times, is established by the fact that in the British Museum there are ornamented vessels of bronze from Nineveh, upon the surfaces of which distinct traces of gold still remain. The expression, *false-silver*, is remarkable, and must have been intended to indicate a metal having a certain degree of resemblance to silver in colour, and probably also in fusibility and hardness. But the only other metals then known, which in colour could be said to resemble silver, were mercury, lead, and tin; and as

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[1] Geschichte der Metalle. Zippe. Wien, 1857, p. 241. An elaborate account of the history of this metal will be found in the following work:—Geschichte des Zinks in Absicht seines Verhaltens gegen andere Körper, etc. G. F. C. Fuchs. Erfurt, 1788.

[2] Derived from Ὀρείχαλκος, compounded of ὄρος, a mountain, and χαλκος, copper.

[3] Lib. xiii. I am indebted to my friend Dr. Smith for the literal translation of this passage, which is quoted by Watson.

[4] Quoted from Watson's Chemical Essays, 1786, 4. p. 85.

these metals may be easily recognized, if any one of them had been intended by the term *false-silver*, it would surely have been designated by its proper name. Moreover, two out of the three, mercury and lead, could not have been intended, because neither would in any degree communicate to copper the properties ascribed to orichalcum.

There are, however, difficulties attending this interpretation of the passage of Strabo. Zinc being very volatile at the temperature at which it is reduced from its ores, the expression *drops* false-silver would seem to be quite inapplicable, unless the furnace to which Strabo refers had, like a modern zinc-furnace, been provided with a suitable distillatory and condensing apparatus; which is extremely improbable. Yet that, in the absence of any special apparatus of this kind, the vapour of zinc may be accidentally condensed in cracks in the walls of a furnace and trickle down in drops, is proved by the fact that I have received from my friend, Mr. Parry, of the Ebbw Vale Iron-Works, specimens of zinc which have thus condensed and trickled down in drops through cracks near the twyers of one of the blast-furnaces, in which a zinciferous ore had been smelted. In regard to the statement concerning "the stone, which, when burnt, becomes iron," and its fusion with a certain earth, there is not a little perplexity. Supposing zinc really to have been indicated by the term *false-silver*, it is doubtful whether the *stone* or the *earth*, or both, yielded the zinc. Various conjectures, more or less plausible, might be offered, which, though interesting in an archæological point of view, would be out of place in this work. Whatever opinion may be entertained as to the interpretation of the passage in Strabo, there is not, I believe, in the works of any other ancient classical author, a single statement which would lead to the inference that the Greeks or Romans had the slightest knowledge of the existence of such a metal as zinc. It is possible that Strabo may have incorrectly described the process of making orichalcum; for in the present day, when travellers possessing no knowledge of metallurgy, though they may be generally well-informed men, attempt to describe, from their own observation, even the simplest metallurgical process, they almost invariably commit great errors, and fail to render an intelligible account. On the other hand, it is not improbable that zinc may have been discovered at a much earlier period than is supposed, as it appears to have been brought from the East by the Portuguese a century before it was produced as a commercial article in Europe, unless we except Goslar, where, according to Lohneiss, it had been obtained prior to 1617.[5] In the early part of the 17th century the Dutch captured a Portuguese ship with a cargo of zinc, which was sold under the name of *speautre*, *spiauter*, *speauter*, or *spialter*: hence the word *speltrum*, introduced by Boyle, and the English word *spelter*, which is almost the only name for zinc in our workshops at the present day.[6] During the last century

[5] Bergman's Physical and Chemical Essays. Trans. London, 1784, 2. p. 313.

[6] Beckmann's History of Inventions. London, 1814, 3. pp. 91-2. Watson's Chemical Essays, 4. p. 2. Watson states that the metal with which this vessel

zinc was largely imported into Europe, under the name of *tutenag*, it is said, from the East Indies.[7]

Several localities in the East are specified from which the metal was procured; and, as China is one of them, and we know that the Chinese possess considerable metallurgical knowledge, it may safely be concluded that zinc was actually produced in China. There is a tradition, moreover, recorded by Bergman, that an Englishman visited China in the last century expressly to learn the art of making zinc; that he attained his object, and returned home in safety with the secret; and that some time afterwards works were erected at Bristol for the extraction of zinc by distillation *per descensum*.[8] By diligent historical research we should probably arrive at positive information on the subject. If we admit that zinc was regularly produced in China as an article of commerce at the period above referred to, it is not unreasonable to suppose that the Chinese practised the art long before that period, possibly in the later times of the Greeks and Romans; and that the metal may have thence found its way into Europe.

In 1721 Henckel published the fact that zinc might be procured from calamine by means of phlogiston, but he concealed the method. In 1742 A. Van Swab extracted it from the ores by distillation, at Westerwick, in Dalecarlia, where it was proposed to erect works to conduct the process on a large scale, but no further step was taken. In 1746 Margraaf, in ignorance of what had been done in Sweden, made known a process of extracting zinc, which he had himself discovered.[9] Dr. Isaac Lawson, in this country, is reported to have first invented a practical method of extracting zinc from calamine, and to have established works for carrying out his invention.[1] Bishop Watson suggests that this Dr. Lawson may have been the man who went to China in order to acquire the art of extracting zinc; but it is merely a suggestion which is entirely unsupported by evidence. According to the same author, zinc-works were first established at Bristol in about the year 1743, by Mr. Champion, who obtained a patent for his process. In 1739[2] a patent was granted to Mr. John Champion for a certain invention relating to metals, but it had no reference to zinc. Again, in 1758,[3] the same person obtained a patent for making spelter and brass from sulphide of zinc or blende, which was known by the names of "black-jack," "mock-jack," or "brazill:" it was directed that the mineral should be washed, purified, ground fine, and calcined; and that the product should be mixed with charcoal and made into spelter, or used as a substitute for calcined calamine in the manufacture of calamine-brass. I find no patent of the date mentioned by Watson; though there can be no doubt from the specification of that last

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was laden was termed calaem, with which he connects the word calamine.

[7] Beckmann, op. cit.

[8] Op. cit., p. 314.

[9] Bergman, op. cit., p. 313. The preceding statements in this paragraph are given on the same authority.

[1] Price, Mineral. Cornub., p. 46. Chambers's Dict., 1753, quoted by Watson, Chem. Ess., 4. p. 36.

[2] Sep. 13. No. 569.

[3] July 28. No. 726.

mentioned, that Mr. Champion had for some time previously been engaged in producing zinc on the large scale. In about the year 1766 Watson visited Mr. Champion's copper-works, near Bristol, and saw the process of making zinc, which at the time was kept rigidly secret. Many years afterwards he published an accurate description of this process, which was the same as that hereafter described as the English process, and which to this day, I believe, is still in operation at Bristol.

Whatever doubt there may be as to the antiquity of the discovery of zinc, there can be none as to the fact that brass—that is, a yellow alloy of copper and zinc—was produced early in the Christian era, if not before its commencement. The proof of this fact is established by the analysis of objects of known date, and may be deduced from descriptions of the process of preparation in works of known date.

Analytical evidence.—Some years ago the Duke of Northumberland presented to the Museum of Practical Geology various coins which had been thrown aside from his collection as duplicates under the inspection of my friend Admiral Smyth. From these I selected for analysis a coin which had a characteristic brass-yellow colour. At my request the late Mr. Burgon, of the British Museum, examined this coin with particular care, and pronounced it undoubtedly genuine. It was a Greek imperial coin of Trajan struck in Caria about A.D. 110, and bearing the name of the magistrate Theodorus. Mr. Burgon was one of the highest authorities on coins of this class. Before the blowpipe it yielded certain evidence of the presence of zinc. It was analysed in my laboratory by Mr. Tookey, and found to have the following composition :—

Copper	77·590
Zinc	20·700
Tin	0·386
Iron	0 273
	98 749

In the collection at the British Museum I examined a coin of Geta struck at Mylasa, in Caria, between A.D. 189–212, which had unmistakably the colour of true brass.

Two other coins containing zinc, from the Northumberland collection, were analysed in the Metallurgical Laboratory some years ago by Mr. T. Philipps. They were examined by Admiral Smyth, who has a high reputation for his knowledge of Roman coins, and who has furnished me with the following descriptions of them. The first was a second brass coin of Vespasian, struck at Rome A.D. 71. Obverse, the profile of Vespasian looking to the right. Reverse, inscription obliterated; a draped female with a cornucopiæ and patera; in the field S. C. (senatus consultu). In the collection of the British Museum I have inspected similar coins which are free from patina, and present the yellow colour of ordinary brass. The second was a large brass imperial Greek coin of Caracalla, struck A.D. 199. Obverse, CEOVHPOC ANTΩNEINOC; the laurelled head of Caracalla. Reverse, obliterated.

Coins of Severus in the British Museum, about 10 years earlier than that here referred to, have a decided brass-yellow colour.

ANALYSES.

	No. 1.	No. 2.
Copper	81·97	74·24
Zinc	18·68	14·42
Tin	..	5·28
Lead	0·14	6·57
Iron	0·12	0·40
	100·91	100·91

Mr. J. A. Phillips has published the following analyses, executed by himself, of ancient coins containing a considerable amount of zinc.[4] Two analyses of each coin were made.

	1.	2.	3.	4.	5.
Copper	82·26	81·07	83·04	85·67	79·14
Zinc	17·31	17·81	15·84	10·85	6·27
Tin	..	1·05	..	1·14	4·97
Lead	..	..	..	1·73	9·18
Iron	0·35	..	0·50	0·74	0·23
	99·92	99·93	99·38	100·13	99·79
Specific gravity	8·52	8·59	8·50	8·30	8·83

No. 1. Large brass of the Cassia family, about B.C. 20; metal of a yellow colour. No. 2. Large brass of Nero, A.D. 60; reverse, Rome seated; metal of a bright yellow colour. No. 3. Titus, A.D. 79; metal yellow and soft. No. 4. Hadrian, A.D. 120; Fortunæ reduci; finely patinated; metal of a fine yellow colour. No. 5. Faustina, jun., A.D. 165; Pietas; without patina; metal of a whitish colour and very brittle.

The two following analyses of Roman coins containing zinc are by Genth.[5] Both were struck, and not cast, and both were very tough:—

	1.	2.
Copper	86·92	88·58
Zinc	10·97	7·56
Tin	0·72	1·80
Lead	1·10	2·28
Iron	0·18	0·29
Silver	0·30	0·21
Arsenic and antimony	traces	..
	100·19	100·72
Specific gravity	8·778	8·754

1. Of the reign of Hadrian; bronze-yellow, but the colour of a fresh fracture inclining to brass-yellow; very finely granular. This analysis agrees pretty closely with that of the coin of the same period by Mr. Phillips. 2. Of the reign of Trajan; colour bronze-yellow,

[4] Quart. Journ. of the Chem. Soc. of London, 1852, 4. p. 252 et seq.

[5] Jahres-Bericht for 1859. Wagner, p. 103.

inclining to brass-yellow; a fresh fracture greyish and very finely granular. Genth remarks that the alloys of which these coins consisted were, "without question," obtained direct from the ores, and that only the small quantity of tin was subsequently added; but this is merely an opinion, which is certainly not beyond question.

Göbel has published the following analysis of a Roman coin containing zinc in the Dorpat Museum: on the obverse is the head of Tiberius Claudius Cæsar, and on the reverse the bust of Antonia Augusta.[6]

Copper	72·20
Zinc	27·70
	99·90

When the so-called brass coins of numismatists contain a considerable amount of zinc, like several of those of which analyses have been given, their colour, to an experienced eye, affords almost conclusive evidence of the presence of that metal. Through the kindness of my friend Mr. Vaux, of the British Museum, I have been enabled carefully to inspect numerous brass coins in the collection under his charge. There are brass coins with the names of Augustus, Drusus, Agrippina, Caligula, and Nero, which have the characteristic colour of true brass. The earliest Roman imperial brass coin of the reign of Augustus has distinctly the colour of true brass. There is a specimen in the British Museum of a piece of rolled metal, under the name of Orichalcum, which was obtained from the melting down of coins of Agrippina and Claudius. In colour and fracture it exactly resembles brass, and before the blowpipe it immediately yields the reactions of zinc. Mr. Vaux showed me a large brass coin of Trajan, struck for Cyprus. The date is A.D. 98–116; on the obverse is the emperor's head, and on the reverse a male figure standing, underneath which is the inscription KOINON KYΠPIΩN. The metal has the characteristic colour of true brass.

Göbel asserts that zinc is only found in alloys of Roman origin, and that the bronze objects derived from the Greeks, and their colonies in Italy, Egypt, Asia, &c., invariably consist of copper and tin, or of these metals and lead.[7]

Descriptive evidence.—In order that this evidence may be appreciated, it is necessary to premise that, until a comparatively recent period, all brass was made by heating metallic copper imbedded in a mixture of calcined calamine and carbonaceous matter. This was effected in large crucibles, which were exposed to a suitable and long-continued heat in furnaces to be hereafter described. The zinc, immediately on its liberation, combined with the copper to form brass.

The account given by Pliny of the metallurgy of copper is incomplete, and, probably, inaccurate; but it is certainly not more unsatisfactory, and cannot be more erroneous, than descriptions of metallur-

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[6] Ueber den Einfluss der Chemie auf die Ermittelung der Völker der Vorzeit | von Dr. Fr. Göbel. Erlangen, 1842, p. 29.
[7] Op. cit., p. 14.

gical processes which are occasionally published in this country at the present day. Much confusion has arisen from the ambiguous sense in which Pliny employs the word cadmia. It is applied by him to a kind of copper-ore (fit et e lapide æroso quem vocant cadmiam) as well as to certain products volatilized during the process of smelting copper. Of these, two distinct varieties are mentioned: one is described as white, and very light (pompholyx); and the other as a solid incrustation upon the walls of the furnace, mixed with sparkling points, and sometimes, also, with charcoal (spodos). These descriptions would be quite applicable to the products formed in furnaces in which zinciferous ores are smelted, or in which any matters capable of evolving metallic zinc are sufficiently heated. The vapour of the zinc would be wholly oxidized, partly within the furnace near the mouth or top, and partly after it escaped into the air, and the result would be the formation of a very light, flaky, white oxide,—which would, as Pliny describes, adhere to the roof of the smelting-house,—and the deposition, in the course of time, of a solid coating, consisting chiefly of oxide of zinc, upon the upper and internal parts of the furnace; and this coating might be more or less crystalline, and present the appearance of sparkling points. We have already seen that zinciferous copper-ores are at this day smelted in Sweden, and that a dense deposit, rich in oxide of zinc, is speedily formed on the sides of the upper part of the furnace.

From the cadmia of the furnaces remedies for ophthalmic diseases were prepared, and compounds of zinc are still applied in the treatment of these diseases. The statements of Pliny concerning the formation and medicinal uses of this artificial cadmia of furnaces are sufficiently corroborated by Dioscorides and other ancient authors.

Now, whatever may have been the ore of copper which, according to Pliny, was termed *cadmia*, to distinguish it from another ore of copper termed *chalcitis*, it seems extremely probable that the *furnace-cadmia* was similar in all respects to the zinciferous incrustations, termed *furnace-calamine*, of modern furnaces; and if these two substances be not identical, I am quite at a loss to conceive of what the ancient *furnace-cadmia* could have consisted. My conviction is that they were identical, for in the smelting of any copper-ores free from zinc no such incrustation would be formed as Pliny describes.

Granting this identity, the word cadmia, as used by Pliny, means both a particular ore of copper and furnace-calamine. But copper-ore is stated by him to furnish cadmia—"metalla æris multis modis instruunt medicinam * * * maxime tamen prosunt cadmia. Fit sine dubio hæc et in argenti fornacibus, etc."[8] In this passage, from the reference to silver-furnaces, it is probable that cadmia refers to furnace-calamine derived from ores of copper, and, if so, it would follow that zinciferous copper-ores were smelted when Pliny wrote. These ores must have been either non-sulphuretted ores or sulphuretted ores. If

[8] Lib. xxxiv. 22.

non-sulphuretted ores, they probably consisted of carbonate of copper in admixture with carbonate of zinc or calamine; and in the smelting of such ores in a small blast-furnace with charcoal, such as the Romans were accustomed to employ, brass, instead of copper, may have been directly produced. But as it would be impossible to prevent the temperature in the lower part of such furnaces from rising sufficiently high to cause the volatilization of much of the reduced zinc, a deposit of cadmia, or furnace-calamine, would be formed on the upper part of the furnace. On the other hand, in the case of sulphuretted ores, the zinc must have existed as blende, and the copper as copper-pyrites, or as some other sulphuretted ore of copper, when the usual process of roasting[9] must have preceded that of smelting; but brass would, probably, not have been directly produced, and difficulties would have occurred such as we have seen have only recently been surmounted in Sweden. Nevertheless this class of ores would have yielded a deposit of cadmia. In either case the copper-smelter would have had at his command metallic copper and cadmia, that is, a substance consisting chiefly of oxide of zinc; and it would have been easy for him to produce brass from these materials by simply heating them together in contact with the fuel of the furnace.

The following passage occurs in Pliny, and much stress has been laid upon it:—"Hoc (æs) a Liviano cadmiam maxime sorbet et aurichalci bonitatem imitatur."[1] The word cadmia in this passage must refer to furnace-calamine: it cannot refer to the ore of copper termed cadmia, as the statement that copper absorbs copper-ore and produces a substance which is not copper, but orichalcum, a metallic substance distinct from copper, would not be intelligible. In the sense of furnace-calamine, and supposing orichalcum in this instance to mean brass, the word cadmia is quite appropriate; and the word "absorbs" exactly expresses what occurs in the preparation of calamine-brass, in which the copper may be truly said to absorb the zinc in proportion as it is reduced.

In another passage concerning the production of *spodos*, a variety of furnace-calamine previously mentioned, it is stated that the Cyprian is the best, and that it is produced in the fusion of cadmia and copper-ore together—"fit autem liquescentibus cadmia et ærario lapide."[2] Admitting cadmia to mean furnace-calamine, and the copper-ore to have been a non-sulphuretted one, brass would certainly have been obtained during this fusion, which was, doubtless, effected in furnaces with charcoal as usual.

There is a third passage in Pliny which, in my judgment, affords strong corroborative evidence in favour of the conclusion that brass was made in his day. In describing the different kinds of copper and its mixtures he writes:—"In Cyprio coronarium et regulare est, utrumque ductile; coronarium tenuatur in laminas taurorumque fello

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[9] The process of roasting on wood is clearly referred to by Pliny in the statement concerning the treatment of the Capuan copper-ores. Lib. xxxiv. 20.

[1] Lib. xxxiv. 2.

[2] Lib. xxxiv. 34.

tinctum speciem auri in coronis histrionum præbet."[3] There were two kinds of Cyprian copper, both ductile; one called "coronarium," and the other "regulare." The former was beaten into thin leaves, of which crowns, having the appearance of gold, were made for actors. The golden tint was produced by colouring the surface of the metal with ox-bile, which would act like a fine yellow lacquer and greatly enrich the colour of ordinary brass. Dr. Bostock remarks[4]—"it is very improbable that the effect could be produced by the cause here assigned." However, that the golden tint mentioned by Pliny would, in a greater or less degree, be produced by the use of bile, I have no doubt; nor do I conceive there would be any difficulty in causing the bile to adhere to the surface of the metal.

It is stated that the German word for native carbonate of zinc, Galmei, and the English word calamine, are derived from cadmia, and, if so, traditional evidence is afforded in favour of the conclusion that the cadmia of Pliny and other early writers contained zinc. But as Pliny applied the term to a particular kind of copper-ore, differing from the ore termed chalcitis, it may be that at an early period a zinciferous variety of this ore happened to be smelted—when the production of furnace calamine would be observed—and that the specific name of the copper-ore became subsequently applied to the product obtained from it by volatilization.

The orichalcum of the ancients has been the subject of much discussion. That this metallic substance differed from copper, and sometimes closely resembled gold in colour, there can be no reasonable doubt. Some writers have, if I am not mistaken, contended that all orichalcum was an alloy of copper and zinc. It seems to me, however, most probable that the term orichalcum included various alloys of copper, of which brass was one. At the present day the terms brass and bronze are constantly used as synonymous, both by public writers and in ordinary conversation, yet they refer to alloys of copper essentially different, brass consisting of copper and zinc, and bronze of copper and tin. Thus, guns composed of *gun-metal*, which is *bronze*, are invariably designated as *brass-guns*. So, also, numismatists apply the term *brass* to coins which do not contain a particle of zinc, but consist wholly of copper and tin. With these facts before us it may easily be imagined that similar confusion in the use of terms prevailed in ancient times, and that orichalcum, like the modern word brass, may have been applied to alloys which in composition differed much from each other.

Festus, who is supposed to have written between A.D. 100 and A.D. 422,[5] seems clearly to indicate that orichalcum was brass; for he

[3] Lib. xxxiv. 20.

[4] Translation of Pliny published by Bohn, p. 189.

[5] Dr. Smith has supplied me with the following note:—"Sextus Pompeius Festus certainly lived after Martial, whom he quotes, and before Macrobius, who quotes him. Martial lived under the emperor Trajan, say A.D. 100; and Macrobius lived under the emperors Honorius and Theodosius, say A.D. 422. Between these two dates, therefore, Festus must have flourished."

states that cadmia was an earth which was thrown upon copper in order to produce orichalcum (Cadmia, terra quæ in æs conjicitur, ut fiat orichalcum).[6] Cadmia is here spoken of as a specific earth, and not as any variety of copper-ore. It is possible that Pliny may have been misinformed, and that the ore of copper, which he states was called *cadmia*, may really have been *calamine* occurring in association with copper-ore.

Ambrose, Bishop of Milan, who lived in the fourth century, has left a description of the mode of preparing what was then called orichalcum; from which it may be certainly inferred that the orichalcum of that day was brass: which, he states, was made by exposing melted copper to the action of certain drugs until it acquired the *colour of gold*.[7] Primasius, Bishop of Adrumetum, in Africa, in the 6th century, and Isidorus, Bishop of Seville in the 7th century, gave similar descriptions of the colour and mode of preparing orichalcum: but Beckmann suggests that these bishops may have copied each other.[8] In the early part of the 11th century, Theophilus, alias Rugerus the Monk, wrote a minute account of the process of making calamine-brass, which was essentially the same as that which has ever since been practised.[9]

From the evidence which has now been advanced, we may, I think, conclude with absolute certainty that the Romans were well acquainted with the art of preparing brass; and that of the various alloys of copper which may have been included under the general appellation of orichalcum, one, and that probably the most highly esteemed, was the yellow alloy of copper and zinc, which we designate brass. Ancient authors who have treated of metallurgical processes appear for the most part to have derived their information from hearsay; and as in all ages, even the present, the workers in metals have generally affected mystery in their operations, it is not surprising that the descriptions of these processes which have come down to us should be incomplete and in a greater or less degree inaccurate.

Calamine was formerly pretty abundant in England, and was exported as ballast. It is stated that in about the middle of the 17th century calamine brass-works were erected in Surrey by Demetrius, a German, at an outlay of 6000*l*., and that a good profit was realized. But British and foreign merchants combined against the proprietor, and involved him in law-suits; and meeting with no encouragement, he was at last ruined, and was compelled to abandon the works, "to the unspeakable prejudice of the kingdom."[1] Calamine brass-works were established in Bristol about 1702, and afterwards at Cheadle in Staffordshire about 1720. I am indebted to my friend Mr. Keates for

[6] Quoted from Watson's Chem. Essays, 4. p. 91.

[7] Quoted from Watson, p. 94. "Æs namque in fornace, quibusdam medicaminibus admixtis, tamdiu conflatur, usque dum colorem auri accipiat et dicitur aurichalcum."

[8] Watson, 4. p. 91; Beckmann, 3. p. 69.

[9] An Essay upon Various Arts, in three books, by Theophilus. Translated, with notes, by Robert Hendrie. John Murray, London, 1847, p. 311.

[1] Some Account of Mines. Heton, London, 1707, p. 154. Heton gives this statement on the authority of Pettus.

the following list of localities where the manufacture has also been carried on :—

Crawhole and Keynsham, near Bristol; Stoke by Stone, Staffordshire; Framilode, Gloucestershire; Greenfield, Flintshire; Macclesfield; Birmingham, where there were two works, of which the last was pulled down about four years ago; Smethwick, near Birmingham; White Rock Works, near Swansea; and subsequently at Llanelly, Glamorganshire. At the works at Smethwick, Swansea, and Llanelly only ingot-brass was made.

Physical Properties.

Colour.—Zinc belongs to the class of white metals, and has a decided bluish-grey tint.

Lustre.—The cleavage-planes on a fresh fracture of an ingot of zinc are very brilliant, especially when the metal is free from iron. Zinc is susceptible of a considerable degree of polish.

Crystalline system.—Nöggerath obtained crystals of pure zinc in the form of regular hexagonal prisms. Plattner also obtained similar crystals from drusy cavities in a large mass of Belgian zinc, which had slowly solidified after fusion.[2] Nicklès states that by the distillation of zinc in a current of hydrogen he procured crystals of the metal in the form of pentagonal dodecahedrons; but as they were not measured, the evidence respecting their form is inconclusive.[3] My friend Professor Miller, of Cambridge, informs me that crystals obtained by sublimation, which he received from Dr. Hugo Müller, are rhombohedral; and that other crystals procured by myself from a drusy cavity in a mass of commercial zinc, which had been melted, with the addition of a small quantity of lead, and afterwards allowed to solidify very slowly, are prisms, the faces of which make with each other angles of about 70° 40′ and 109° 20′. These crystals have some other faces which are too imperfect to afford satisfactory measurements, so that he cannot venture to say whether they belong to the prismatic, oblique, or anorthic system. My friend Professor Cooke, of Harvard College, U.S., has described octahedral crystals of the cubical system, which consisted of 81·18 per cent. of zinc, and 18·82 of arsenic.[4] Professor Miller has examined these crystals, and confirmed the statement respecting their form. Professor Cooke remarks that "the quantity of arsenic in these crystals is so much smaller than the amount required to form any probable definite compound, that there can be but little doubt that it is present as impurity, and that the octahedrons are an isomorphous mixture of the two elements. The presence of a certain amount of impurity seems to favour metallic crystallization; and it is possible that it may be the disposing cause in this case, inducing, as it were, a monometric condition of the zinc." That the crystalline form of zinc may

[2] Berg. u. hütten. Zeit., 1853, p. 14.
[3] Ann. de Chim. et de Phys., 1848. 3. s. 22, p. 37.
[4] American Journ. of Science and Arts, 1861, v. 31.

be modified by the presence of other metals, which may be regarded as foreign matter, seems probable; but further experiments are necessary to establish the fact that arsenic has the power of causing zinc to crystallize in the cubical system. Although, from the foregoing statements, zinc would appear to be dimorphous, yet additional evidence is required to justify a decided conclusion on the subject.

Hardness.—It is a comparatively soft metal, though much harder than tin: it clogs the file.

Malleability and ductility.—At the ordinary temperature an ingot of commercial zinc may be easily broken in pieces. The metal flattens somewhat under the hammer, and is very much less brittle than bismuth or antimony. At 200° C. zinc is so brittle that it may be easily reduced to powder by trituration; but between 100° C. and 150° C. it is sufficiently malleable to admit of being rolled into thin sheet and drawn out into fine wire. The malleability of zinc also depends, in a certain degree, upon the temperature at which it has been melted: when cast near the temperature of its melting-point, it is more malleable than when cast at a higher temperature.[5] Bolley has ascertained that when pure zinc is cast at a low temperature, it is much more rapidly acted upon by acids than when cast at nearly a red heat. Zinc is considerably hardened by the process of rolling, especially if it contains a sensible amount of iron, but the hardness may be removed by careful annealing at a *low* temperature; whereas it has been previously stated (p. 7) that soft sheet-zinc becomes brittle after exposure to a temperature bordering on its melting-point. The discovery that zinc is malleable when gently heated is comparatively recent, and since that time the rolling of zinc has become a manufacture of considerable importance. Sheet-zinc is now applied to a great variety of useful purposes, such as roofing, spouting, &c., while in former times the metal was only employed in alloy with copper.[6]

Fracture.—The fracture of an ordinary ingot of zinc presents numerous, very distinct, and brilliant crystalline surfaces set at various angles, and more or less foliated; but considerable variation may be observed in the fracture of different samples of commercial zinc: in some it is much more confusedly crystalline than in others, which present comparatively large, even, crystalline faces. Bolley has shown that the structure of an ingot of zinc is modified in a striking degree by the temperature at which the metal is cast. When pure zinc is only just heated to the temperature of its melting-point, then poured, and allowed to cool slowly after solidification, its fracture is finely granular; whereas, if previously to pouring it is heated nearly to redness, its fracture is always largely crystalline. So long as the metal is

[5] Mentzel, Karsten's Archiv. 1829, 1. p. 417.

[6] A patent was granted, A.D. 1805, to Charles Sylvester and Charles Hobson for "a method of manufacturing the metal called zinc into wire and into vessels." The metal is directed to be drawn or rolled at a temperature of from 210° F. to 300° F. (99° C. to 148° C.). Abridgments of the Specifications relating to Metals and Alloys, 1861, p. 39.

poured at the higher temperature, the rate of cooling, whether slow or extremely rapid (as when it is allowed to flow in a fine stream into ice-cold water), has but little effect: the fracture will always be largely crystalline.[7] Bolley suggests that, if zinc be dimorphous, this difference of structure may possibly depend on a difference in the crystalline form of the metal in the two cases mentioned.

Specific gravity.—Bolley has investigated this subject in a very satisfactory manner, and has proved that the variation which has been observed in the specific gravity of zinc after fusion is entirely due to the diffusion of minute cavities through the metal. It nearly always occurred that the same piece of zinc weighed entire gave a lower specific gravity than portions of it obtained by fracture; and not unfrequently Bolley detected small cavities as large as a pin's head in the cut or fractured surfaces of cast zinc. He was only enabled to arrive at results, which nearly approximated, by weighing the metal in small particles produced by fracture, and not by filing; for he found that air adhered so tenaciously to zinc filings that in boiling them in water loss by projection was liable to occur. The zinc upon which Bolley operated was cast in moulds or cases of sheet-brass, from 2 to 3 inches wide, and about 5 inches high. They were fixed in an inclined position, and after receiving the metal were somewhat shaken. When it was desired that the metal should cool slowly, they were placed in hot sand; and when the contrary was desired, they were surrounded with a mixture of snow and water, having been coated externally first with tinfoil and then with collodion, in order to render them water-tight. Only the lowest part of the ingots were selected for examination, and the average weight of each piece operated on was 10 grammes. The following results were those obtained by repeating the weighings with smaller and smaller pieces of metal until at length they were less than peas, and the weights found in two successive weighings agreed well with each other. The observations were made at 12° C.

Specific gravity of zinc poured at a temperature near its melting-point:—

Rapidly cooled—Mean of seven observations..... 7·178
Extremes, 7·201, and 7·155.
Slowly cooled—Mean of eight observations ..... 7·145
Extremes, 7·191, and 7·061.

Specific gravity of zinc poured at nearly a red-heat:—

Rapidly cooled—Mean of eight observations ..... 7·109
Extremes, 7·179, and 7·030.
Slowly cooled—Mean of six observations ..... 7·120
Extremes, 7·171, and 7·030.

Matthiessen found the specific gravity of zinc free from arsenic to be 7·148 at 15° C. Three determinations were made with the re-distilled metal, the pieces being re-fused after each. The results were 7·144 at 15°5, 7·150 at 14°4, and 7·149 at 15°.[8] According to Karsten the spe-

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[7] Zur Kenntniss der Molecularеigenschaften des Zinks. Von P. A. Bolley. | Ann. der Chem. u. Pharm. 1855, 95. p. 294.

[8] Philos. Trans. Dec. 22, 1859, p. 163.

cific gravity of rolled commercial zinc is 7·1908, and after hammering and rolling it may even reach 7·2 or 7·3.

Tenacity.—It is stated by Berthier that zinc wire 0^m002 (0·0784 inch) in diameter breaks under a weight of about $12^{kil.}$ (26·455 lbs.).[0]

Specific heat.—0·09555 between 0° C. and 100° C. (Regnault).

Dilatation by heat.—The coefficient of the linear dilatation between 0° C. and 100° C. is stated to be 0·000029412,[1] whilst that of the cubic dilatation was found by Kopp to be 0·000089.[2] According to the first statement zinc increases $\frac{1}{340}$ in length when heated from 0° C. to 100° C.

Action of heat.—According to Person the melting-point of commercial zinc is 434° C., and that of re-distilled zinc 433·3° C.[3] Daniell stated the melting-point of zinc to be 412° C. A much lower melting-point was given by former observers. At a bright red heat zinc may be readily distilled.

Certain Chemical Properties of Zinc.

Atomic weight.—32·53, Erdmann.

Action of oxygen.—At the ordinary temperature zinc is not acted upon by *dry* oxygen; but when exposed to moist oxygen or to atmospheric air, its surface acquires a compact, tenacious, grey coating of hydrated oxide, which impedes the oxidation of the subjacent metal. In this respect the rust of zinc differs much from the rust of iron, which, instead of impeding, seems rather to accelerate the oxidation of the subjacent metal. By the conjoint action of moist oxygen and carbonic acid, zinc is converted into a hydrated carbonate. It is stated that zinc is not acted upon when exposed to moist air free from carbonic acid, so long as it does not become bedewed or actually moistened.[4] The rust produced by the action of atmospheric air on zinc roofing has been found by Pettenkofer to consist of $5ZnO + 4CO^2 + 8HO$. The roofing from which the specimen analysed was obtained had been exposed to the atmosphere of Munich for 27 years. Pettenkofer ascertained that during that period 8·381 grammes of zinc per square foot (Bavarian) had been oxidized, and that nearly half of the oxide is carried off by rain. Hence he estimated that a layer of zinc only 0·005 of a line in thickness, requires, in the atmosphere of Munich, 27 years to be entirely corroded: so that, leaving out of consideration the oxidation of the lower surface which may practically be disregarded, a zinc roof of 0·25 of a line in thickness would be completely corroded in 1243 years. The roof would, however, long previously become quite useless![5] When melted zinc is exposed to the air at the temperature of, or not much exceeding, its melting-point, its surface becomes speedily covered with a grey pellicle, which is renewed as fast as it is removed, so that by repeated stirring the whole of the metal may be converted

[0] Tr. des Essais, 2. p. 563.
[1] Berthier, 2. p. 563.
[2] Liebig u. Kopp. Jahresb. 1851, p. 55.
[3] Ann. de Chim. et de Phys. 1848, 3. s. 24, p. 136.
[4] Bonsdorff, Répertoire de Chimie Scient. et Indust. Paris, 1838, 4. p. 165.
[5] Chem. Gaz. 1857, p. 478.

into a grey powder. Berzelius regards this powder as a definite sub-oxide of zinc, whereas, in the opinion of some other chemists, it is merely a mixture of oxide of zinc and the finely-divided metal. When zinc is exposed to the air in a state of fusion, at a temperature sensibly exceeding its melting-point, or, according to Daniell, at 505° C., it takes fire and burns with a bright bluish-white flame, forming oxide of zinc, of which part remains as a crust on the surface of the burning metal, and part is carried upwards into the atmosphere in the form of extremely light snow-like flakes, formerly designated *nil album*, or *lana philosophica*. The metal, when once ignited, will continue to burn with flame after the crucible, in which the experiment may be made, has been removed from the furnace, provided the crust of oxide on the surface be constantly removed by stirring. The whole of the metal may thus be converted into oxide. Oxide of zinc is practically fixed, and the fumes which arise when melted zinc burns in the air are caused by the combustion of the volatilized metal. Neither the vapour of the metal nor its oxide is poisonous.

Oxide of zinc: Formula ZnO.—It was formerly known by the names of *pompholyx*, *tutia*, and *flowers of zinc*. It usually occurs as an amorphous powder, which is white when cold and yellow when hot. Hence the fumes of this oxide, on escaping from the chimneys of furnaces in which brass is melted, have a fine yellow colour. A peculiar and characteristic odour is perceived during the combustion of zinc. Oxide of zinc is occasionally found as a metallurgical product crystallized in hexagonal prisms of the rhombohedral system. Berzelius states that it is always yellow when crystallized or fritted by exposure to a high temperature;[6] but according to G. Rose, crystals of *pure* oxide of zinc are perfectly white.[7] Diesel is of opinion that pure oxide of zinc may be either yellow or white, according to the state of aggregation; and that the yellow variety becomes white by sufficient exposure to a high temperature.[8] It is infusible *per se*. Berthier states that it is fixed, and Gmelin that it is volatile at a white heat. To determine which of these statements is correct, the following experiment was very carefully made (S.)[9]:—Oxide of zinc was prepared by the combustion of the metal, and of this 19·5 grains were enclosed in a crucible made of platinum foil, which was put into a small Stourbridge clay crucible, and heated during 1½ hour to the highest temperature which could be obtained in a small muffle, and which was that of whiteness. The clay crucible was softened and flattened down: the particles of oxide were very feebly sintered together, and the mass crumbled under slight pressure between the fingers. The loss in weight was 0·75 grain, or about 3½ per cent. The oxide was yellow on the external

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[6] Tr. de Ch. 1846, 2. p. 611.

[7] Das krystallochemische Mineralsystem, 1852, p. 65.

[8] Liebig u. Kopp, Jahresb. 1851, p. 355.

[9] I am desirous of acknowledging to the fullest extent the aid which I have received from my colleague, Mr. R. Smith, and yet I am not willing to obtrude the name so frequently as I have hitherto done on the attention of the reader. I shall, accordingly, employ the initial letter S. as an abbreviation for the entire name.

surface where it was in contact with the platinum, but remained white within. It was prepared in the manner stated, with a view to provide against the possibility of error from the presence of foreign matter. In order to arrive at a satisfactory result, it is necessary to heat the oxide in an atmosphere which is certainly *not reducing*, a condition which cannot be well ensured except in a muffle furnace. The experiment was repeated under exactly the same conditions upon 16·435 grains of the oxide which had been heated in the last experiment: the loss amounted to 0·100, *i.e.*, 0·608 per cent. At the lower part the oxide had a greenish yellow colour, and was much more coherent than elsewhere. The surface of the mass of oxide was yellow as before, and the platinum in contact with it appeared to have been slightly acted upon, as it was duller than on the external surface, which retained its original brightness. Oxide of zinc is insoluble in water, but soluble in aqueous solutions of potass, soda, ammonia, and carbonate of ammonia. According to Berthier, it is insoluble after calcination in ammonia or carbonate of ammonia; but this is an error. Oxide of zinc is a powerful base; it also forms combinations with the alkaline earths and several bases; and it has a strong affinity for alumina. When a solution of oxide of zinc in ammonia is mixed with a solution of alumina in potass, a compound of alumina and oxide of zinc is precipitated.[1] It combines with water, and the formula of the hydrate is ZnO,HO: the water is entirely expelled at a red-heat. Oxide of zinc becomes green when moistened with nitrate of cobalt and heated before the blow-pipe in a non-reducing flame. It is extensively employed as a white pigment, and as an ingredient in pottery colours. Professor Cooke, of Harvard College, U.S., informs me that in America oxide of zinc is largely prepared by reducing the ore in reverberatory furnaces of a peculiar construction, burning the vapour of zinc evolved by means of a blast, and conducting the products of combustion into large chambers of moistened canvas. The uncondensable gaseous matters escape through the canvas, while the oxide of zinc is retained within it.[2]

Zinc heated with powerfully oxidizing solid reagents.—Violent deflagration occurs when finely-divided zinc is heated with nitre, chlorate of potass, or arsenic acid, oxide of zinc being formed: in the last case metallic arsenic is evolved.

Action of water on zinc.—At ordinary temperatures water has no action on zinc, provided air be excluded; but when zinc filings are moistened with water and left exposed to the air, the mass after some time acquires a dark colour and increases in volume; hydrogen gas is evolved with visible effervescence, and the metal is ultimately converted into grey oxide.[3] At a red-heat zinc readily decomposes the vapour of water. If the experiment is made in a porcelain tube *strongly* heated, the zinc as it volatilizes is converted into oxide, which is deposited on the sides of the tube in small, brilliant crystals

[1] Berzelius.

[2] The use of "a porous or fibrous bag or air chamber with porous sides" for this purpose is claimed in a patent granted A.D. 1850. No. 13192.

[3] Berzelius, Tr. de Ch. 2. p. 607.

of a vitreous lustre; but if the tube is *less strongly* heated, the drops of metal become coated with very pretty small crystals of oxide.[4] When commercial sheet zinc is boiled in water from which air has been previously expelled by boiling, hydrogen is very slowly evolved just below 100°C.; and on continuing the experiment during one or two hours the action decreases. This point was examined by A. Dick in my laboratory. The zinc employed was well cleaned with emery paper, and the hydrogen was collected in an inverted tube.

Zinc heated with protoxide of lead.—The following experiment was made (S.):—

Ratio of mixture.		Quantities employed, in grains. Zinc in fine powder.	Litharge.
Zn, 2PbO	=	160	1120

The mixture was heated in a well-covered clay crucible to a strong red heat during three-quarters of an hour: the products were a button of malleable lead weighing 245 grains, and a dark brown resin-like slag imperfectly melted in the centre, and containing shots of metal. The proportion of lead reduced is nearly the same as Berthier obtained in a similar experiment.[5]

Zinc heated with the fixed alkaline carbonates.—The carbonic acid is decomposed with the formation of carbonic oxide and oxide of zinc.

Zinc heated with the neutral fixed alkaline sulphates.—The sulphuric acid is said to be decomposed with the formation of oxide and sulphide of zinc.

Zinc heated with carbonic acid, (S.)—Dry carbonic acid was passed over zinc in a tube of hard glass heated to redness, when carbonic oxide was copiously evolved, and burned at the end of the tube from which it escaped. Brilliant, minute crystals of zinc were found deposited on the upper surface of the tube, each apparently consisting of an agglomeration of crystals similar to those described by Nicklès, and erroneously believed by him to be pentagonal dodecahedrons.

Reduction of oxide of zinc by carbon and carbonic oxide.—The oxide is reduced by either of these agents at a strong red-heat; and, conversely, metallic zinc at a red-heat reduces carbonic acid to carbonic oxide; but, so far as is yet known, it has no action on carbonic oxide at any temperature, even the highest. In order that complete reduction should be effected by carbon, it is not necessary that the oxide of zinc and solid carbonaceous matter should be intimately mixed. On the large scale oxide of zinc in a greater or less degree of purity is always the compound from which zinc is directly extracted; and carbonaceous matter, such as charcoal, coal, or coke, is always employed as the reducing agent. Frequently both the oxide and reducing agent are in the state of coarse particles, and are *very imperfectly* mixed. The contact, therefore, between these two matters is very imperfect, and yet complete reduction takes place; so that it is certain that carbonic oxide must be actively concerned in the process. The operation is effected in large clay vessels. The interstices between

[4] Regnault, Ann. des Mines, 3. s. 11. p. 16.

[5] Tr. 1. p. 384.

the particles are filled with atmospheric air, of which the oxygen becomes speedily converted into carbonic oxide, as there is always a large excess of carbonaceous matter. The oxide not in direct contact with solid carbonaceous matter is reduced by carbonic oxide, with the formation of carbonic acid, which is instantly converted into carbonic oxide by contact with the surrounding incandescent carbonaceous matter; for otherwise the reduction of the oxide of zinc would speedily cease, as metallic zinc at the temperature at which it is liberated reduces carbonic acid to carbonic oxide with the formation of oxide of zinc. The limited quantity of carbonic oxide existing in the first instance in the reducing vessel, acts as a vehicle by means of which the carbon is brought in contact with the oxide of zinc: it is perpetually being converted into carbonic acid and re-converted into carbonic oxide. A current, therefore, of carbonic oxide and of the vapour of zinc will continue to escape during the whole period of the reduction. If any reduced zinc should happen to be re-oxidized by the carbonic acid generated, the oxide of zinc formed, being light and finely divided, would necessarily be brought in direct contact with solid incandescent carbonaceous matter, and be immediately reduced.

Reduction of oxide of zinc by hydrogen.—Experiment by A. Dick, in my laboratory. A current of hydrogen, after having been exposed successively to the action of sulphuric acid, chloride of calcium, and hydrate of potass in fragments, was passed over oxide of zinc heated to redness in a tube of hard glass. At first the oxide seemed to volatilize, only a small quantity of metallic zinc being visible; but on sending a *good* current of gas through the tube, reduction took place rapidly. However, a little of the reduced zinc was evidently again oxidized in the vapour of water formed, and was carried forwards as a white sublimate. The metallic zinc condensed in small drops in the cooler part of the tube; and although these drops must have consisted of comparatively pure zinc, yet they were found to dissolve with brisk effervescence in dilute sulphuric acid. Deville states that when 10 or 15 grammes of pure oxide of zinc are exposed to the action of a feeble current of pure hydrogen at a very high temperature in a porcelain tube, no reduction takes place: there is merely a change in the position of the oxide of zinc, which is deposited in other parts of the tube in well defined and occasionally large crystals. When, however, the oxide is exposed under precisely the same conditions to a rapid current of hydrogen, reduction occurs, and metallic zinc appears in the tube. In explaining these results, Deville entirely discards the so-called *action of mass:* "otherwise," he writes, "at the moment when the vapour of water and zinc react upon each other to reproduce oxide of zinc and hydrogen, this gas being predominant in the mixture ought, by reason of its mass, to protect part of the metal from oxidation. This never happens when the operation is conducted with sufficient slowness. But all is explained by admitting that variation in temperature causes the affinities to be reversed: thus, in the part of the porcelain tube heated directly, zinc in vapour and water may well coexist; but in parts less heated, where the zinciferous deposit occurs, affinities

change, water is decomposed, and every trace of metallic zinc disappears. This takes place in my experiments: but when the hydrogen passes with rapidity, the zone of the tube in which the reverse action occurs is traversed by the mixture of the vapours with such rapidity that the cooling of the matters prevents the ulterior reaction." [6] Concisely stated, Deville's explanation is that at a given temperature hydrogen reduces oxides of zinc, and at a lower temperature zinc decomposes water. Let us call the higher temperature *a*, and the lower temperature *b*. Now, if there be no action of mass, as Deville supposes, it would necessarily follow that at *a* oxide of zinc should be reduced by exposure to a small quantity of hydrogen in admixture with a large quantity of the vapour of water; and that at *b* metallic zinc should decompose the vapour of water in admixture with a large quantity of hydrogen. But Deville has not adduced any experimental evidence to show that these results occur under the conditions supposed. That the action of mass should not be ignored in these phenomena of reduction seems evident from the experiments previously recorded (p. 15), as also from the conclusive reasoning of Gay-Lussac on the reducing action of carbonic oxide. Although it is well known that affinities are affected by temperature, yet it appears to me that the phenomena of reduction for which Deville accounts by a change of affinity consequent on a change of temperature are also perfectly explained by the difference in the relative proportions of hydrogen, the vapour of zinc and the vapour of water consequent on the difference in the velocity of the current of hydrogen in the two cases under discussion.

Sulphur heated with oxide of zinc.—It is stated that sulphide of zinc is formed, and sulphurous acid evolved.

Iron heated with oxide of zinc.—The oxide is reduced by iron at a high temperature, and the whole of the zinc is volatilized.

Oxide of zinc heated with silica.—The following experiments were made (S.) on the direct formation of silicates of zinc by strongly heating intimate mixtures of oxide of zinc and fine Australian sand of great purity :—

Ratio of mixture.		Quantities employed in each experiment, in grains. Oxide of zinc.	Sand.
1. ZnO, SiO^3	=	200	230
2. $2ZnO, SiO^3$	=	240	138
3. $3ZnO, SiO^3$	=	240	92
4. $3ZnO, 2SiO^3$	=	180	138

Results.—1. The mixture was exposed in a Cornish crucible in a muffle during five hours to a strong heat at or near whiteness. The product was fritted. The frit was pulverized and reheated under precisely the same conditions as in the first firing. The second product, though more strongly fritted than the first, was yet not melted. 2. The mixture was heated under precisely the same conditions, and during the same time as No. 1. The product was fritted,

[6] Ann. de Chim. et de Phys. 1855, 3. s. 43, p. 479.

but not so firmly as No. 1. 3. The mixture was heated under precisely the same conditions, and during the same time as No. 1. The product was fritted, not quite so firmly as No. 1, but more so than No. 2. 4. The mixture was heated under the same conditions as No. 1 during 3½ hours. The product was slightly fritted, but readily crumbled between the fingers: it had a yellowish white colour. A portion from the centre of the frit obtained in the first three of the foregoing experiments was heated in a crucible of platinum foil during two hours in a muffle furnace; the platinum crucible was placed within a covered clay crucible, and protected from contact with the walls of this crucible by supports of platinum wire. The heat was quite *white*, and the outer clay crucibles were softened and flattened. Similar experiments were attempted in Deville's furnace, when the platinum was melted, possibly from having been attacked by zinc reduced by the gases of the furnace. 1. No sensible change. 2. Fused, slightly porous, opaque, translucent at the edges, fracture vitreous in lustre, white, with a very slight yellow tinge. 3. Fused, of a greenish yellow tint, more translucent than, but in other respects similar to, No. 2.

Native hydrated silicate of zinc, nearly pure, was perfectly melted by exposure in a crucible of platinum foil under the same conditions, when it was converted into a mass which was opaque, stony, and greenish grey in colour.

Gelatinous silica was separated by the action of hydrochloric acid on each of these products, so that in every case silicate of zinc had been formed.

In the Great Exhibition of 1851 were exhibited, in the French Department, specimens of beautiful colourless glasses, composed of silica, oxide of zinc, and alkaline or earthy bases.

Silicate of zinc heated with carbon.—The following experiments were made (S.):—(1.) 20 grains of artificial silicate of zinc of the formula $3ZnO, SiO^3$, produced as above described, were mixed in the state of powder with 5 grains of charcoal. The mixture was put into a small covered brasqued crucible, such as are used in the Swedish method of assaying iron ores, and this crucible was enclosed in a covered plumbago crucible, the space between the two being filled with anthracite powder. The mixture was exposed to a white heat during 1 hour. The residue in the brasqued cavity was very light, porous, and friable; it occupied the same space as the original mixture; it did not gelatinize with hydrochloric acid; it was fused with mixed carbonates of potash and soda, and the product was carefully tested for zinc, but no trace was detected; it contained, however, a little oxide of iron and carbon. Supposing the oxide of zinc to have been completely reduced and the zinc evolved, the residue of silica should have weighed 5·54 grains, whereas the actual weight was 6·3; but the difference may be accounted for by the oxide of iron and carbon in the residue. (2.) 20 grains of calcined nearly pure native silicate of zinc were mixed with 5 of charcoal, and the mixture was treated exactly like that in No. 1. The residue weighed 6·5 grains, and after ignition 5·1, the

decrease being due to the removal of a little carbon with which it had been mixed; it did not gelatinize with hydrochloric acid, nor could a trace of zinc be detected in it by the method of testing adopted in No. 1. The experiment was repeated with exactly the same result. (3.) 50 grains of the same finely-powdered native silicate of zinc were treated under precisely the same conditions in a brasqued crucible without admixture with charcoal. The residue was porous, somewhat slagged on the exterior, and weighed 13·86 grains; it was quite free of zinc. (4.) 130 grains of the same native silicate in *small pieces*, about as large as peas, were heated without admixture with charcoal in a brasqued crucible, under the same conditions as those above described; the residual pieces were agglutinated at the edges, weighed 44 grains, and contained zinc. The conclusion to be drawn from these experiments is that oxide of zinc, in finely-divided silicate of zinc, may be completely reduced by exposure to a high temperature in a brasqued crucible, even without having been mixed with charcoal.

Silicate of zinc heated with lime and charcoal, (S.)—The native hydrated silicate from the United States was employed; it was tested, and found to be nearly pure, containing only a trace of iron and lime. An intimate mixture of 50 grains of calcined native silicate of zinc, 50 grains of lime, and 20 of charcoal, was heated in a brasqued and luted crucible during an hour in an iron-assay furnace at the highest temperature. The residue gelatinized by the addition of hydrochloric acid, and evolved a small quantity of sulphuretted hydrogen, but contained no trace of zinc.

Oxide of zinc heated with boracic acid.—The following experiments were made (S.):—

Ratio of mixture.		Quantity employed in each experiment, in grains. Oxide of zinc.	Fused boracic acid.
1. ZnO, BO^3	=	200	175
2. $2ZnO, BO^3$	=	240	105
3. $3ZnO, BO^3$	=	240	70
4. $3ZnO, 2BO^3$	=	240	140

The ingredients were intimately mixed and heated in a covered platinum crucible to strong redness in a muffle during about half an hour. In every case perfect fusion occurred, and the products, which were very liquid, were poured into an open iron ingot mould.

Results.—1. The product solidified into a colourless, transparent glass, slightly opalescent on the external surface; the fracture was conchoidal and non-crystalline. 2. The product, when solid, was white, vitreous, crystalline, and translucent; the fracture was largely lamellar, and had a beautiful pearly lustre. 3. The product, when solid, was vitreous, pale yellow, and opaque in mass, but translucent in small pieces; the fracture was less largely lamellar than that of No. 2, and had a more or less pearly lustre. 4. The product was a beautiful, perfectly transparent and colourless glass, presenting no trace of crystallization.

By the addition of a small quantity of boracic acid, tribasic silicate

of zinc was rendered perfectly fusible, as will appear from the following experiment (S.) :—

A mixture of oxide of zinc, silica, and boracic acid was prepared according to the formula

$$3\,(3ZnO,\ SiO^3) + 3ZnO,\ BO^3.$$

The proportions taken were—oxide of zinc 240 grains, fine sand 69 grains, and fused boracic acid 17½ grains: this corresponds to 5·37 per cent. of boracic acid. The mixture was at first heated in a covered platinum crucible to redness in a muffle, when the product was found to be merely fritted. The frit was then heated under the same conditions to whiteness during half an hour: the product was perfectly melted, and solidified into a white, translucent mass, of which the fracture was largely crystalline, and had a pearly, or rather adamantine, lustre.

Oxide of zinc heated with alumina.—(S.)—An intimate mixture of oxide of zinc and anhydrous alumina, in the ratio of 1 equivalent to 6, was heated in a small covered crucible of platinum foil, enclosed in a covered and luted clay crucible during an hour, in Deville's furnace. The outer clay crucible was softened and flattened. The mixture was agglutinated into a compact, grey, stony substance, which scratched flint-glass. The quantities operated on were 1·6 grain of oxide of zinc and 12 grains of alumina.

Oxide of zinc heated with protoxide of lead.—When oxide of zinc is heated with eight times its weight of litharge, a very liquid product is formed, which is crystalline like litharge, in very small laminæ, opaque, and of a very pale yellow colour. But when it is heated with only six or seven times its weight of litharge, the product has a pasty consistency.[7]

Oxide of zinc heated with the fixed alkaline carbonates.—Fusible compounds are obtained; but in order that they should be thoroughly liquid, a high temperature (50° Wedgwood's pyrometer) must be employed, and the oxide of zinc at most should not exceed ¼ of the weight of the mixture. The melted product is homogeneous, crystalline, translucent, and colourless.[8]

Oxide of zinc heated with cyanide of potassium.—Oxide of zinc mixed with a large excess of cyanide of potassium was exposed in a tube of hard glass, closed at one end and drawn out at the other after the introduction of the mixture to the highest temperature of a blowpipe air-gas flame. The fused product had while hot the yellow colour of oxide of zinc; no trace of vapour of zinc was observed to escape from the drawn-out end of the tube, (S.)

Sulphide of zinc: Formula ZnS.—Precipitated from an aqueous solution of a salt of zinc by sulphuretted hydrogen or a soluble sulphide, sulphide of zinc is an amorphous, white powder, which, heated in a close vessel, loses water, and acquires a pale yellow colour. It

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[7] Berthier, Tr. 1. p. 515.

[8] Ibid., Tr. 2. p. 567.

becomes crystalline and agglomerated by exposure to a strong white heat, or at a temperature at which wrought iron may be easily melted: but it may be said to be *practically* infusible. When a mixture of finely divided zinc and sulphur is projected into a red-hot crucible, combination takes place with incandescence; but much of the metal may be preserved from the action of sulphur by becoming coated with infusible sulphide of zinc. When a mixture of zinc turnings and cinnabar is suddenly exposed to a strong heat, detonation occurs like that produced by heating a mixture of a combustible substance and nitre, sulphide of zinc being formed, and the mercury reduced and volatilized. At a lower temperature the greater part of the cinnabar sublimes. When a mixture of zinc filings or granulated zinc and polysulphide of potassium is heated, as soon as the latter melts, sulphide of zinc is formed with violent deflagration.

Blende appears to be somewhat volatile at very high temperatures without fusion. The following experiment was made (S.):—200 grains of pulverized Laxey blende, free from matrix, were heated in a small Stourbridge clay crucible in Deville's furnace during 1½ hour: anthracite was the fuel employed, and the temperature was extremely high. The crucible containing the blende was closed with a well-fitting cover, over which was placed an inverted crucible; and the two crucibles thus arranged were put into a plumbago crucible, over which was also placed an inverted clay crucible. The blende became firmly agglutinated, though not fused, into one mass, and lost 9 grains in weight. The upper part of the interior of the crucible containing the blende and the under surface of the cover were coated with dark crystalline matter, of a somewhat metallic lustre; but none was found in the interior of the inverted crucible immediately above. Precipitated sulphide of zinc was exposed in a small covered clay crucible, enclosed in a well-covered and luted plumbago crucible, to the highest temperature of an iron-assay furnace during an hour. At the upper part of the inner crucible, around the edges of the cover, a ring of matter was deposited perfectly crystalline, translucent, of a fine brown colour, and in lustre exactly resembling common blende: at the bottom of the crucible was a small somewhat porous mass, perfectly crystalline, of a light brown colour, and having the lustre of blende. There was a considerable space between this mass and the adjacent walls of the crucible, which were sensibly acted upon and fused into a dark brown glass. On the internal surface of the crucible above were numerous small clusters of minute, brilliant, brown, translucent crystals, some of which appeared to be sharply defined hexagonal prisms, with flat ends. This is the form of oxide, and not of sulphide, of zinc. Yet, according to Breithaupt, oxide and sulphide of zinc have the same crystalline form, and the so-called oxysulphide of zinc, which occurs as a furnace product, is isomorphous with them.[9] In another experiment, in which Laxey blende in powder

[9] Berzelius, Jahres-Ber. 1841, 20. p. 84.

was very strongly heated in a clay crucible covered with a piece of fire-brick and luted, the under surface of the brick acquired a brown colour, and presented very numerous minute, brilliant, brown crystals, similar to those above described, sparingly interspersed with brilliant, dark brown, glass-like globules. The brick was penetrated to a slight depth with these crystals. The crucible was put into the furnace enclosed in a covered plumbago crucible. The precise conditions under which these hexagonal prisms were formed have not yet been clearly ascertained. The sublimation of blende in blast furnaces has already been particularly mentioned.

Sulphide of zinc heated with other sulphides.—According to Berthier, sulphide of zinc combines with most of the metallic sulphides, though with difficulty; and the combinations which it forms are only slightly fusible. He found that at the temperature of 60°, Wedgwood's pyrometer, the following mixtures were softened and agglomerated, but not liquefied:—

	Parts by weight.			
Sulphide of zinc	1	1	1	1
Protosulphide of iron	1	..	1	..
Galena	..	1	1	..
Sulphide of antimony	..	..	..	2

Sulphide of zinc is a constituent of various kinds of regulus. It tends to diminish fusibility, as in the case of the *skumnas* formerly produced at Åtvidaberg.

Sulphide of zinc heated with access of air.—When sulphide of zinc in a finely divided state is roasted at a gentle red-heat, sulphurous acid is freely evolved, with the formation of oxide and sulphate of zinc; and by suitably raising the temperature towards the end of the process, the sulphate will be wholly decomposed, and only oxide of zinc will remain. At a tolerably strong red-heat sulphate of zinc is completely decomposed; nearly the whole of the sulphuric acid is resolved into sulphurous acid and oxygen, only a little fuming acid being produced. The residue consists of light oxide of zinc, which retains only a trace of sulphuric acid. Deville suggests the use of this salt as an economical substitute for peroxide of manganese in the preparation of oxygen.[1] Zinc is now largely extracted from the native sulphide of zinc or blende, which it is necessary to convert as completely as possible into oxide by the process of roasting. But of all the sulphides with which the metallurgist has to deal, sulphide of zinc is one of the most troublesome to roast *sweet*. It has, however, the advantage of not clotting by heat, so that in the process of roasting it may from the first be exposed to a much higher temperature than most other sulphides.

Sulphide of zinc heated with oxide of zinc.—According to Berthier there is no decomposition, and the oxide combines with the sulphide in all proportions to form compounds, fusible at high temperatures. A crystallized

[1] Ann. de Chim. et de Phys. 1861, 3. s. 61, p. 123.

substance forming an incrustation (Ofenbruch) in one of the Freiberg furnaces was examined by Kersten, and pronounced to be oxysulphide of zinc of the formula $ZnO + 4\,ZnS$, which is that of the native mineral Voltzine. This product was occasionally light yellow, foliated, adamantine in lustre, and contained transparent hexagonal prisms from ¼ to ¾ inch in length. Berzelius justly remarks that the formula in question could not be certainly deduced from the data obtained by Kersten.[2]

The following experiments were made in clay crucibles lined with blende, (S.) The crucibles were filled with Laxey blende in powder, solidly rammed down, closed with well-luted covers, and then strongly heated during about half an hour. The blende becomes thereby firmly agglutinated, so that cavities may be easily made in it.—(1.) 40 grains of oxide of zinc were put into a blende cavity, which was then filled up with powdered blende. The crucible was enclosed in a covered plumbago crucible, and exposed during 1 hour to a white-heat. When quite cold the inner crucible was examined. That part of the blende cavity which had been filled with oxide of zinc was found to be quite empty, and to be considerably acted upon towards the bottom. The substance of the clay crucible was coloured blue. (2.) 20 grains of oxide of zinc were intimately mixed by trituration with 72 of Laxey blende, *i.e.* in the ratio of $ZnO : 3ZnS$. The mixture was treated exactly like No. 1. A light porous crystalline residue, weighing 60 grains, and resembling blende, was found in the blende cavity. Supposing decomposition to have taken place with the liberation of zinc, and an equivalent proportion of sulphurous acid, as represented in the equation $2ZnO + 6ZnS = Zn^2 + SO^2 + 5ZnS$, the residue of blende should weigh 60 grains, *i.e.* the actual weight found. (3.) A mixture of 40 grains of oxide of zinc and 48 of sulphide, *i. e.* in the ratio of $ZnO : ZnS$, after having been heated in the same manner, gave a residue similar to that in No. 2, which weighed 22 grains. Supposing the same reaction to have occurred as in No. 2, the residue should have weighed 24 grains. (4.) A mixture consisting of 40 grains of oxide and 24 of blende, *i. e.* in the ratio of $2ZnO + ZnS$, after having been heated in the same manner, gave a very light residue weighing 4·2 grains, from which only a trace of oxide of zinc was dissolved by heating with ammonia. In this experiment the oxygen of the oxide of zinc was just sufficient to form sulphurous acid with the sulphur of the sulphide. The covers of the inner crucibles in all these experiments were coated on the under surface with minute brilliant crystals of various shades of brown. The preceding results seem to establish the fact that, contrary to what has hitherto been asserted, oxide and sulphide of zinc mutually reduce each other at high temperatures, just like oxide and disulphide of copper at much lower temperatures. Numerous trials were made in the first instance with clay crucibles not lined with blende, but in no case could a decisive result be obtained, as the substance of the crucible was always much corroded.

[2] Jahres-Ber. 1831, 10. p. 119.

Sulphide of zinc heated with carbon.—When sulphide of zinc is subjected to a white heat, either in admixture with charcoal or simply in a brasqued crucible, it wholly disappears, and is probably decomposed, with the formation of bisulphide of carbon. When the experiment is made with native blende containing iron, there is a residue of sulphide of iron perfectly free from zinc, (S.)

Sulphide of zinc heated with various metals, (S.)—*Iron.*—Complete reduction occurs at a bright red heat; the zinc being wholly volatilized, and sulphide of iron formed. *Tin.*—The following experiments were made: A mixture of 96 grains of pulverized Laxey blende and 116 of finely-granulated tin, *i.e.*, in the ratio of 1 equivalent to 1, was exposed in a covered clay crucible to a bright red-heat during half an hour. The product consisted of a button of metal covered with regulus, which was easily detached from the former. The button weighed 14·5 grains; it was harder than tin, yet flattened considerably under the hammer, but not without slightly cracking at the edges; its fracture was crystalline-granular, and had nearly the colour of tin; it contained zinc. The regulus weighed 11 grains; it was hard, brittle, finely-granular in fracture, and iron-grey in colour. Great volatilization, therefore, both of zinc and tin occurred, the former probably in combination with sulphur. The internal surface of the crucible was not acted upon, and there was no sign of permeation. The experiment was repeated with a mixture of 192 grains of blende and 232 of tin, *i.e.*, in the same ratio as before; the crucible was exposed to the same degree of heat as in the last experiment, but during a longer time, namely, three-quarters of an hour. The result was similar. The button of metal weighed 16·5 grains. The regulus could not be detached from the crucible and weighed. Both metal and regulus resembled those of the last experiment. *Antimony.*—The following experiments were made: A mixture of 144 grains of Laxey blende and 120 of antimony, *i.e.*, in the ratio of 3 equivalents to 1, was prepared by trituration, and exposed in a covered clay crucible to a bright red-heat during half an hour. The product consisted of an agglutinated and firmly-coherent mass; it weighed 245 grains, so that the loss amounted only to 19 grains; it was easily fractured, when the mass appeared to consist of a uniform mixture of particles of blende and a well-melted metal, resembling antimony; under particular directions of incident light, the fracture taking place in one plane, the lustre was brilliantly metallic. The whole of the internal surface of the crucible above the mass at the bottom, as well as the under-surface of the cover, was lined with minute metallic particles, partly globular and partly crystalline, over which were deposited here and there small radiating groups of minute white acicular crystals. The experiment was repeated with the same results. Hence, antimony does not appear to reduce sulphide of zinc, even at a high temperature. *Lead.*—The following experiment was made: A mixture of 192 grains of pulverized Laxey blende and 416 of finely-granulated lead, *i.e.*, in the ratio of 1 equivalent to 1, was exposed in a covered clay crucible at a bright red-heat during three-quarters of an hour. The product was an

imperfectly-fused cavernous mass; it was hard, brittle, largely crystalline, dark lead-grey, and metallic in lustre. Not a trace of metallic lead was found. The whole of the internal surface of the crucible was considerably acted upon and melted into a brown porous substance; the under-surface and edges of the cover were coated with metallic matter resembling galena in fracture. *Copper.*—Two experiments were made, with the following proportions:

Ratio of mixture.		Quantity employed, in grains. Laxey blende.	Copper in powder.
1. ZnS + 2Cu	=	48	64
2. ZnS + 4Cu	=	48	128

The mixtures were exposed in covered clay crucibles to a bright red-heat during half an hour.

Results.—1. The product consisted of a button of metal covered with regulus. The metal resembled copper in colour and other respects: it weighed 15 grains. The regulus resembled disulphide of copper, and weighed 67 grains. The internal surface of the crucible and cover was covered here and there with numerous small globules, similar in appearance to the regulus. 2. The product consisted of a button of metal and regulus. The metal resembled yellow brass in colour and fracture: it weighed 85 grains. The regulus resembled disulphide of copper, and weighed 71 grains. Hence, sulphide of zinc is reduced by copper at a high temperature. The proportion of zinc remaining alloyed with the copper will necessarily vary with the degree of heat and duration of the experiment.

Sulphide of zinc heated in hydrogen.—According to Berthier it is not acted upon when heated in hydrogen.[3]

Sulphide of zinc heated in the vapour of water.—Regnault obtained the following results: When native sulphide of zinc or blende is heated in a glass tube in a current of aqueous vapour, a small quantity of sulphuretted hydrogen is evolved; but after the experiment had continued during two hours, the blende had scarcely changed in appearance. When, however, the experiment was carried on at a strong heat in a porcelain tube, decomposition was much more easily effected, and the blende was almost completely desulphurized, oxide of zinc being deposited in small silky masses in that part of the tube from which the steam escaped.[4]

Sulphide of zinc heated with carbonic acid, (S.)—Dry carbonic acid was passed over blende in small pieces about as large as peas in a porcelain tube heated to redness. The experiment was continued during 2 hours, and the gas was collected over mercury: it was wholly absorbed by a solution of potass, so that no reduction could have taken place. Possibly reduction may be effected at a much higher temperature.

Sulphide of zinc heated with protoxide of copper.—The following experiments were made (S.): the mixtures were exposed to a strong red-heat during half an hour in covered clay crucibles:—

[3] Tr. 2. p. 569.

[4] Ann. des Mines, 3. s. 11, p. 46.

Ratio of mixture.		Quantity employed in each experiment, in grains. Laxey blende.	Protoxide of copper.
1. ZnS + 2CuO	=	120	200
2. ZnS + 3CuO	=	144	360

Results.—1. The product consisted of a button of metal and regulus, covered with a ring of vitreous brown-black slag: the surface of the crucible in contact with this slag was corroded. The metal was like copper, had a dull fracture, and weighed 70 grains. The regulus resembled disulphide of copper in appearance, and weighed 106 grains; it was tender, easily detached from the button of metal, finely granular in fracture, bluish-grey, and had moss-copper on its surface. 2. The result was similar. The button of metal weighed 201 grains, and the regulus 30 grains.

Sulphide of zinc heated with protoxide of lead.—Both elements of the sulphide are oxidized with the formation of sulphurous acid, which escapes, oxide of zinc, and metallic lead. According to Berthier, sulphide of zinc requires to be mixed with not less than 25 times its weight of litharge, in order that the oxide of zinc formed may be perfectly dissolved in the excess of litharge. When these proportions are employed, the resulting slag is vitreous, resin-brown, with an olive tint in colour, and translucent at the edges; and 28 per cent. of pure lead is reduced. Berthier strongly heated a mixture of 24·08 gram. of blende and 55·78 gram. of litharge, *i.e.*, in the ratio of 1 equivalent to 2; 29·2 gram. of very hard (aigre) lead of a greyish-black colour separated: it contained 1·8 per cent. of sulphur and 0·8 of zinc and iron. The button of lead was covered by a black, somewhat metallic matter, intermediate between a regulus and a slag, and which consisted of sulphides and oxides of zinc and lead.[5]

Sulphide of zinc heated with peroxide of manganese.—According to Berthier, decomposition takes place at a white heat with the formation of sulphurous acid, oxide of zinc, and protoxide of manganese. In attempting to determine this reaction by experiment we failed to obtain satisfactory results on account of the corrosion of the clay crucibles employed.

Sulphide of zinc heated with nitre or nitrate of soda.—The action is energetic, both elements of the sulphide being oxidized with the formation of oxide of zinc and sulphuric acid, which remains in combination with the alkaline base.

Sulphide of zinc heated with carbonate of potass or soda.—According to Berthier, at a red-heat chemical action takes place with effervescence, but there is no disengagement of metallic zinc: the product is well melted, homogeneous, opaque, and light brown. When carbonate of soda is heated with sulphide of zinc in the ratio of 1 equivalent to 1, the product contains oxide of zinc, sulphide of zinc, and sulphide of sodium, and no sulphuric acid; but as the sulphide of sodium in the product contains more sulphur than the monosulphide, a portion of the zinc would appear to be oxidized at the expense of the car-

[5] Tr. 1. p. 403.

bonic acid of the alkaline carbonate, with the formation of carbonic oxide. When the same experiment is made with the addition of charcoal, oxide of zinc is not produced, but an equivalent proportion of metallic zinc is volatilized.[6]

Sulphide of zinc heated with lime.—Berthier states that lime decomposes sulphide of zinc, but only with the aid of carbon. The amount of zinc volatilized increases with the temperature. He exposed a mixture consisting of 6·03 grammes of sulphide of zinc and 6·32 of carbonate of lime (*i. e.*, in the ratio of 1 equivalent of each) to an extremely high temperature (150° Wedgwood's pyrometer) in a brasqued crucible. More than $\frac{4}{5}$ of the zinc volatilized, and there remained a spongy, friable button, crystalline in grain and of a slightly yellowish white colour; it only weighed 4·60 grammes, and contained but very little sulphide of zinc.[7] This result is obviously not conclusive as regards the direct action of lime on account of the presence of carbon, which reduces sulphide of zinc at a high temperature. The following experiment was made (S.): 35 grains of Laxey blende, very pure, and containing 66 per cent. of zinc, were heated in intimate admixture with an equal weight of lime in a lime crucible, closed with a lime cover, and placed within a covered plumbago crucible filled up with fragments of lime. The crucibles thus arranged were exposed during an hour to the highest temperature of an iron-assay furnace. At the bottom of the lime crucible was a small, very porous, imperfectly-melted, and light brownish lump, which was more or less isolated, but at the bottom adhered firmly to the lime; it weighed 27 grains. By the action of boiling water some soluble sulphide was extracted. It dissolved in hydrochloric acid with the evolution of sulphuretted hydrogen, and the solution contained a little zinc. The lime in the vicinity of this lump was coloured grey, apparently by the permeation of some matter. The lime crucible and the fragments of lime were rendered black by the permeation of matter from without.

Zinc and carbon.—It is stated that commercial zinc almost always contains carbon in combination. Quite recently Eliot and Storer have accurately investigated this point: in several kinds of zinc they failed to obtain decided evidence of the presence even of a trace of carbon; while in others they never found "more than an infinitesimal amount of carbon in the considerable residue" left after the solution of 30 or 40 grammes of the metal in acids. According to Berzelius, a carbide of zinc is produced by heating cyanide of zinc in close vessels.[8]

Zinc and phosphorus.—Combination takes place when phosphorus is dropped upon melted zinc. According to H. Rose, when a mixture of 2 parts of zinc and 1 of phosphorus is heated in a luted glass retort, a sublimate is produced having a metallic lustre, silver-white colour, and vitreous fracture. Zinc containing phosphorus is stated to resemble lead in colour and lustre, to be somewhat malleable, to emit the odour of phosphorus when filed, and to have nearly the same fusibility as zinc. I find that when an intimate mixture of equal weights of pul-

[6] Tr. 2. p. 569. [7] Ibid. p. 570. [8] Ibid. p. 616.

verized amorphous phosphorus and finely divided zinc is heated, combination takes place without glowing, and a dark grey mass of agglutinated particles is obtained, which does not melt at a red-heat: by the action of hydrochloric acid on this mass, phosphuretted hydrogen, not spontaneously inflammable, is disengaged. A strong odour of this gas is evolved when the phosphuretted zinc is breathed upon; and when the metal is heated before the blow-pipe, it ignites with flame, and continues to burn like tinder. Phosphorus seems to diminish the fusibility of zinc in a striking degree. When the mixture of phosphorus and zinc is heated in a clay crucible, its substance throughout acquires a grey colour. In 1848 Mr. A. Parkes obtained a patent, in which, amongst various things, he claimed the addition of phosphorus to zinc and its alloys;[9] but I am not aware that any practical application of phosphorized metal or alloys has been made. The brilliancy of zinc was said to be increased by treatment with phosphorus, which may possibly have acted by effecting the removal of any iron in the state of phosphide.

Zinc and arsenic.—They combine directly by the application of a gentle heat. There is much discrepancy in books concerning the fusibility of the alloys of zinc and arsenic. Berthier states that by heating in a porcelain retort equal parts of arsenic and metallic zinc, an alloy is produced, which is grey, brittle, granular in fracture, and *fusible at a white heat!*[1] I have made the following experiments on this point: An intimate mixture, prepared by triturating together 132 grains of zinc and 75 of arsenic, *i. e.*, in the ratio of 4 equivalents to 1, was heated in a glass tube closed at one end, when, at a temperature considerably below a red-heat, combination, attended with a red glow, was effected. The product was a coherent mass of the form of the tube; its external surface was bright in parts which had been in immediate contact with the glass; it was tolerably coherent, but broke under the hammer, the blows of which very sensibly indented the surface; the fracture was quite *sui generis;* it was dark grey, minutely porous, irregularly granular, and presented the appearance of the agglutination of particles without perfect fusion. A portion of the product was exposed in a covered clay crucible for some time to a good red-heat, but without fusing or changing its form; the same portion was again subjected to a strong red-heat during about half an hour, and with the same result, except that on fracture it appeared somewhat more porous. By exposure to a bright red-heat the alloy, if made with pure zinc, may be wholly volatilized, and apparently without previous fusion. A mixture of zinc with 10 per cent. of arsenic was prepared, and treated as in the last experiment: combination was effected without sensible glow, and the product closely resembled that just described; it was more coherent, and flattened rather more under the hammer, but it had not fused, and the character of its fracture was the same as before. Melted zinc readily takes up arsenic, and in proportion to the quantity of arsenic added becomes solid and com-

[9] A.D. 1848, Nov. 11. No. 12325.

[1] Tr. des Ess. 2. p. 572.

paratively infusible. By the action of hydrochloric or dilute sulphuric acid on zinc containing arsenic, arseniuretted hydrogen is evolved. This gas when inhaled is a deadly poison, and the lives of two chemists at least have been destroyed by it. Death, attended with great suffering, occurs in the course of a day or two after the inhalation. The warning cannot be too often repeated, that of all the compounds of arsenic this is one of the most insidious and poisonous.

ORES OF ZINC.

1. *Red zinc ore, or oxide of zinc.*—This mineral consists essentially of oxide of zinc, and owes its colour to the accidental presence of a small quantity of oxide of manganese, which, estimated as MnO^2, has been found in five different specimens to vary in amount from a trace to about 12 per cent. It is found and raised in New Jersey, U.S., where zinc-works have been erected for its treatment. By exposure to the atmosphere its surface becomes converted into pulverulent carbonate. It contains distinct traces of arsenic.[2]

2. *Carbonate of zinc or calamine*, ZnO, CO^2.—When pure it contains 52·02 per cent. of zinc. Carbonates of the following bases have been found in crystallized calamine from different localities: lime, magnesia, protoxides of iron, manganese, lead, copper, and cadmium. Native calamine varies much in purity, and is frequently found in admixture with sesquioxide of iron, carbonate of lime, sulphate of baryta, clay, and electric calamine or hydrated silicate of zinc. The proportion of cadmium in calamine does not seem to have been sufficiently investigated. According to the following analysis by Long, the calamine of Wiesloch in Baden contains rather more than 2 per cent. of cadmium[3]:—

Carbonate of zinc	89·97
,, cadmium	3·36
,, lime	2·43
,, magnesia	0·32
,, protoxide of iron	0·57
Oxide of zinc	2·06
Water	0·35
Residue	0·45
	99·51

In five analyses of the Wiesloch calamine by Riegel, previously published, there is no mention of cadmium.[4] Calamine occurs in the Devonian, carboniferous, and oolitic formations, in veins, beds, and large deposits or pockets. In England it appears to have been formerly raised in considerable quantity in Somersetshire, Derbyshire, and Cumberland, having, as previously stated, been exported as ballast;

[2] On the Impurities of Commercial Zinc, with special reference to the Residue insoluble in Dilute Acids, to Sulphur, and to Arsenic. By Charles W. Eliot and Frank H. Storer.—Memoirs of the American Academy of Arts and Sciences, New Series, vol. viii. 1860.

[3] Quoted from Leon. Jahrb. 1858, in Rammelsberg's Handb. der Mineralchemie, 1860, p. 1019.

[4] Bischof. Lehrb. der Chem. u. Phys. Geolog. 1855, 2. p. 1883.

but in 1859 it is recorded that only about 285 tons of calamine were raised in the United Kingdom—248 tons from Cumberland, and 37 tons from Ireland.[5]

Towards the end of the last century about 1500 tons of calamine were annually raised in Derbyshire, and sold at about 2*l.* per ton, or about 6*l.* 6*s.* when thoroughly dressed. At the same period the calamine from the Mendip hills in Somersetshire sold for 8*l.* per ton when dressed.[6]

On the Continent there are numerous well-known localities of calamine, amongst which may be particularly mentioned the vicinity of Liège in Belgium, Silesia, and Carinthia, where the extraction of zinc has long been carried on. Recently large and valuable deposits of calamine have been discovered in the north-west of Spain, in the Asturias, in the vicinity of Santander, and in Biscay.

3. *Hydrated silicate of zinc, or electric calamine*, 2 ($3ZnO, SiO^3$)+3HO. —In some mineralogical works this mineral is described under the same name as common calamine or carbonate of zinc, and confusion is apt to arise in consequence. Thus, the name Smithsonite is applied to it in Brooke and Miller's edition of 'Phillips's Mineralogy,' while in Dana's Treatise the same name is applied to carbonate of zinc. Silicate of zinc is generally, if not always, associated in a greater or less degree with carbonate of zinc. My friend Professor Brush, of Yale College, U.S., informed me in 1859 that it had begun to be employed in the United States as an ore of zinc, and that the zinc extracted from it was purer than the best Silesian and Belgian varieties.

4. *Sulphide of zinc, blende, or black-jack*, ZnS.—When pure it contains 67·03 per cent. of zinc. It decrepitates strongly when heated. Pure blende is a mineralogical rarity: the white and colourless variety of New Jersey, U.S., was analysed by the late Mr. T. H. Henry, and found to be absolutely pure, with the exception of a trace of cadmium: its sp. gr. was 4·063.[7] Blende nearly always contains a considerable quantity of sulphide of iron. In 13 out of 16 analyses of blende from different localities recorded by Rammelsberg, iron is present in proportions varying from 1·18 to 18·1 per cent.[8] Copper occasionally occurs in blende, but less than 1 per cent. in amount. Cadmium is a frequent, if not a general, constituent of blende; and it is probable that its presence has been overlooked in many analyses. As much as 1·78 per cent. of cadmium has been found in blende from Przibram, in Bohemia,[9] and 3·2 per cent. in blende from Eaton, New Hampshire, U.S.[1] Blende from the King William Mine, at Clausthal, contains, according to Kuhlemann, 0·63 per cent. of antimony, 0·79 of cadmium, and 0·13 of copper, besides 1·18 of iron.[2] Blende is met with in association with galena, iron pyrites, and copper pyrites, from which it should always be *dressed* as clean as possible. Blende is occasionally argentiferous, and sometimes sufficiently so to allow of the profitable extrac-

[5] Mineral Statistics of the Geolog. Survey of Great Britain, 1860, p. 48.
[6] Watson's Chem. Ess. 1786, 4. p. 8.
[7] Phil. Mag. 1851, 4. s. 1. p. 23.
[8] Handb. der Mineralchem. 1860.
[9] By Löwe. Rammelsberg, op. cit.
[1] By Jackson. Dana, 1854, p. 45.
[2] Liebig u. Kopp's Jahresb. 1856, p. 832.

tion of the silver. Plattner states that blende occasionally contains traces of tin and manganese.[3]

Blende occurs in numerous localities in Europe. In 1859 about 13,000 tons were raised in the United Kingdom, and of this amount Wales supplied about 5500 tons, Laxey, in the Isle of Man, 2500 tons, Cornwall 2400 tons, and Derbyshire 1500 tons, the remainder having been raised in Devonshire and Ireland.[4] A large supply of blende might be derived from Sweden; and recently the Vieille Montagne Company has obtained a concession of mines of blende in that country.[5] The price of blende has risen enormously in this country of late: a few years ago Laxey blende was usually sold at from 23*s.* to 26*s.* per ton; whereas recently one firm has paid as much as, if not more than, 4*l.* 4*s.* per ton for this ore.

Blende is a German word, derived from the verb *blenden*, to dazzle, which is said to have been applied to this sulphide on account of its bright or dazzling lustre. Watson records the fact that in his time the miners sometimes succeeded in selling to inexperienced smelters black-jack instead of lead ore.[6] It would, I think, be difficult to find any lead-smelter of the present day so unwary as to be thus imposed upon!

ENGLISH PROCESS OF EXTRACTING ZINC.

In the historical notice of zinc, this process has been referred to. The reduction is effected in large pots closed at the top, and having an opening at the bottom through which the vapour of the zinc is conducted into a chamber underneath, where it is condensed and collected. Several of these pots are heated in a furnace constructed on precisely the same plan as an ordinary circular glass-house furnace. Although the process is generally known as the English process, yet I am by no means sure that it is an English invention. I shall describe the process as I saw it conducted near Swansea in 1848, and near Neath in 1859. The accompanying woodcuts have been executed from sketches and measurements taken by myself in 1859. Blende was the ore employed.

Roasting or calcination of the blende.—When the ore is not delivered at the works in a sufficiently fine state of division, it is crushed between iron rolls, so that it may pass through a sieve of 5 or 6 holes to the inch. After crushing it is washed to separate earthy matter. It is roasted on a flat-bedded calciner, in the construction of which there is nothing peculiar. The charge is 16 cwt., of which the roasting is completed in twenty-four hours with the consumption of about 2 tons of coal. It requires to be well stirred at intervals. The loss in weight by roasting is about 20 per cent.; but it will necessarily vary with the nature of the ore. Some years ago in an establishment near Swansea, where the English reduction process was in operation, double-bedded calciners were heated successfully by the waste heat of

[3] Die Probirkunst. Leipzig, 1853, p. 330.

[4] Mineral Statistics, 1860, p. 48.

[5] My authority for these statements is Mr. A. Grill, to whose father-in-law these mines belonged.

[6] Essays, 4. p. 5.

the reduction furnace. One bed was built over the other; each bed was 10 feet long and 6 wide; and there was a hole, through which the ore could be transferred from the upper to the lower bed. A charge of 5 cwt. of ore was spread over the upper bed, on which it was roasted at a red-heat during twelve hours. It was then raked up, and let fall through the hole above-mentioned upon the lower bed, where it was exposed to a much stronger heat during twelve hours more, the flame passing directly from the furnace over the lower bed, and from thence over the upper bed.

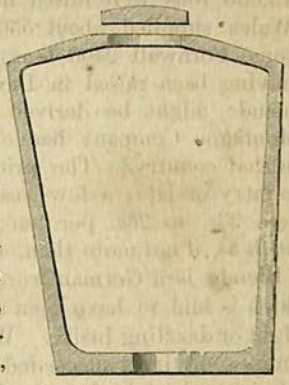

Fig. 122.

Pots and condensing tubes.—A vertical section through the centre of a pot is shown in fig. 122, to double the scale of figs. 124, 125. The transverse section is circular. There is a circular opening at the top, through which the charge is introduced. Around this opening the outer surface is flat, to receive the cover, which is shown above the pot in fig. 122. At the bottom of the pot is also another but smaller opening. The condensing arrangement consists of two tubes of sheet-iron $\frac{1}{16}$ of an inch thick; an upper and short one, *a*, and a lower and long one, *b*. The tubes are simply made by folding the iron, and roughly riveting together the overlapping edges. The short tube is conical, tapering downwards; around its upper edge is a ring of flat bar-iron, *c*, forming a flange. The ring is kept in its place by indenting the tube from within; it is very roughly made, and the ends did not even meet in some tubes. Below is another ring of bar-iron, *d*, which is loose, and of a diameter such that it may not be pushed higher than seen in the figure. The flange, *c*, is pressed firmly in contact with the bottom of the pot, so that the centre of the hole may

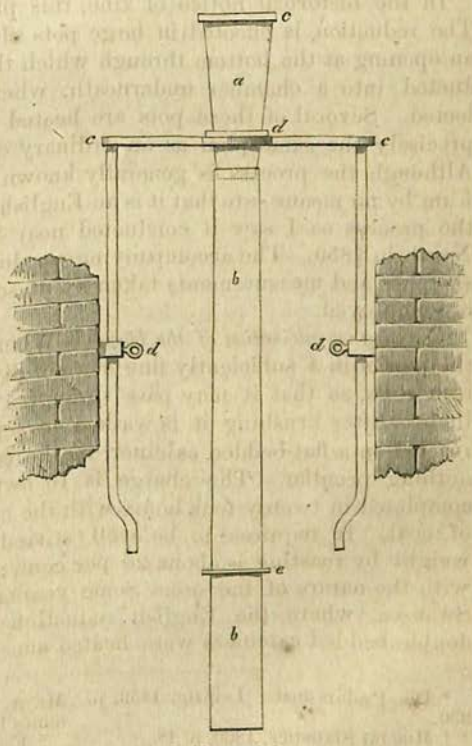

Fig. 123. Scale double that in figs. 124, 125.

coincide with that of the tube. This short tube is firmly fixed by means of the cross rod of iron, *c*, *c*, in the middle of which is a ring, as indicated by the shading; at the ends of this rod are the iron rods, *d*, *d*, which pass through pieces of iron provided with screws, and let into the side walls. The lower tube is conical, and widens downwards; its upper end fits on the outside of the lower end of *a*, and by giving it a twist round, it hangs suspended. At *e* is a ring of iron riveted on, which serves as a handle. The lower tubes frequently drop off, but may be immediately readjusted. Underneath the lower end of each long tube is placed a vessel of sheet-iron to receive the zinc as it drops. The complete adjustment of the tubes is shown in B, fig. 125.

Reduction house.—It consists of two stories, the upper one, A, in which the pots are heated, and the lower one, B, called the *cave*, fig. 125,

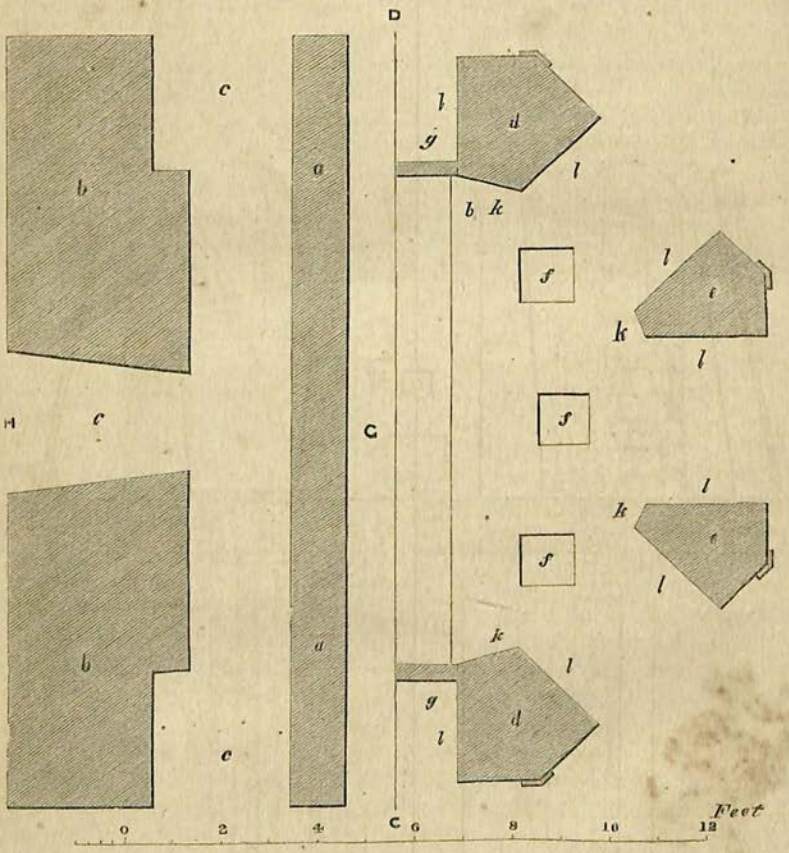

Fig. 124.

in which the zinc is condensed. The furnace is octagonal. Fig. 124, on the left of the line C, D, is a ground plan of half the furnace, and on the right of the same line is a plan of half the furnace on the line E, F,

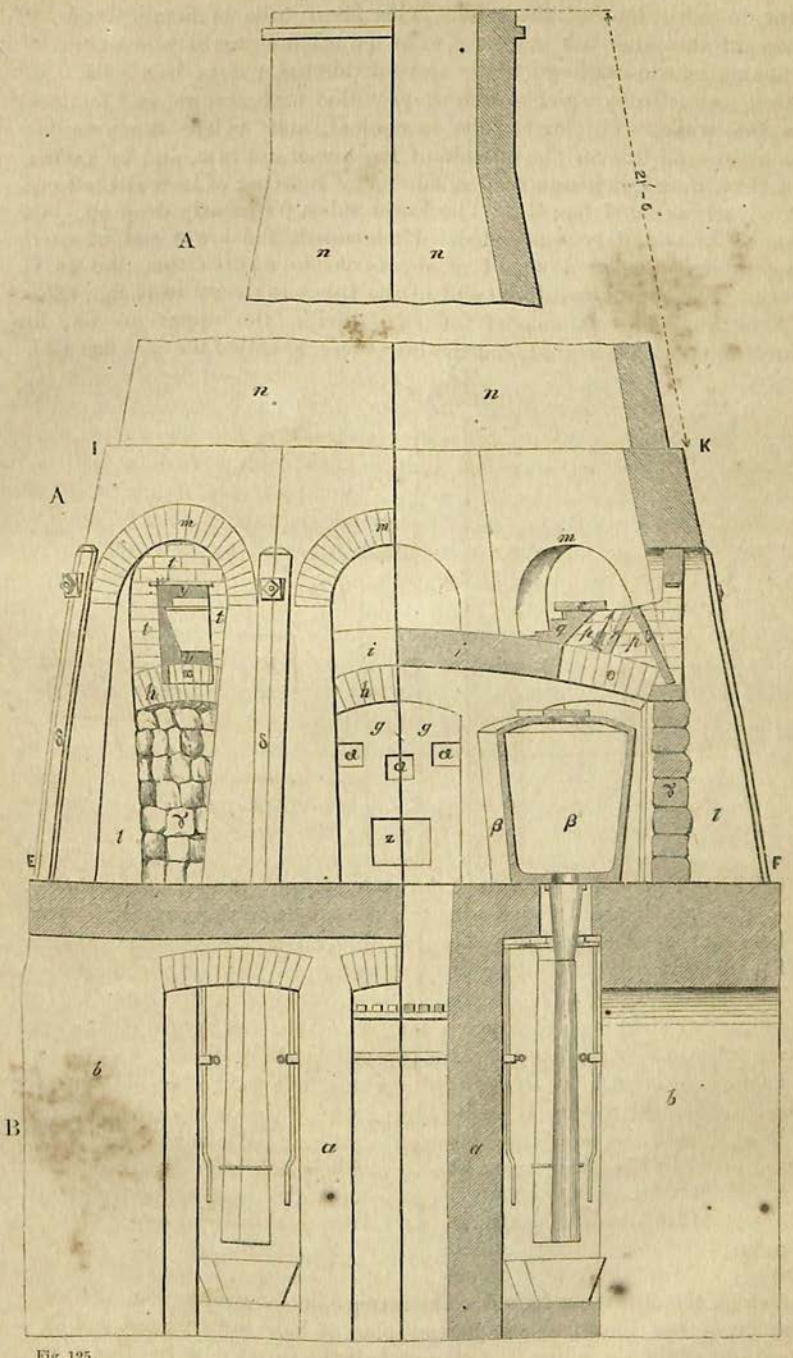

Fig. 125.

in the elevation, fig. 125, which is the floor-level of the upper story. As the furnace on each side of the line C, D, is in all respects similar, it was not considered necessary to represent more than half of it. The foundation in the cave is contained within a square, of which the side is 16 feet. *b*, *b*, are vertical piers of brick: *c*, *c*, *c*, are spaces by which the condensing tubes can be conveniently reached; they are arched over near the top of the cave. There is one of these spaces for each set of tubes. From the floor of the upper story rise eight piers, of which four are shown at *d*, *d*, *e*, *e*. The fire-place extends across the furnace from *g* to *g*; on each side of it is a flat bed of fire-brick on a level with the floor. In this bed are six holes, each 13 inches square, three on each side, *f*, *f*, *f*, which communicate with the cave below. Over these holes the pots respectively stand. The bed of this part of the furnace is supported by bars of iron, which pass from the upper part of the wall, *a*, *a*, to the opposite piers, *b*, *b*, fig. 124. On the left of the vertical central line in A, fig. 125, is shown half the furnace in elevation; and on the right of the same line is shown the other half in section on a line passing through the middle of the fire-place at right angles to its long axis. *Externally*, the piers *d*, *e*, *e*, *d*, incline inwards up to the plane, passing through the line I, K; and from this plane springs the cone *n*, *n*, *n*, *n*, which becomes cylindrical near the top. This cone carries off the smoke of the furnace. The piers are united above by the arches *m*, *m*, *m*. *Internally*, the piers *d*, *e*, *e*, *d*, are vertical as high as the arches *h*, *h*, of which they form the abutments. Between every two adjacent piers is a similar arch, so that there are eight in all, of which those at the ends of the fire-place, *g*, *g*, are somewhat narrower than those on each side. From the piers on a level with the abutments of the arches, *h*, *h*, springs the flat dome or roof, *i*, *i*, which covers in the furnace; the rise of this dome is only 9 inches. The spaces, *g*, *g*, under the arches at the ends of the fire-place, are closed with vertical walls of brick, in each of which is a fire-hole, *z*, and three smaller holes, *a*, *a*, *a*, which are stopped with bricks easily movable; through these holes any cracks which may occur in the pots on the sides towards the fire-place may be filled up by plastering on clay with a long tool. The fire-hole has no door, and is kept stopped with coal piled up against it. Through the open spaces under the side arches, *h*, the pots are introduced and fixed, so that the centre of the hole at the bottom may coincide with the centre of the square hole in the bed; the spaces are then closed by walls built of large rough pieces of brick, *γ*, *γ*, and in each of these walls are adjusted easily movable bricks, which are indicated by the shading in the elevation, and which are intended for a similar purpose as those at *a*, *a*, *a*. In the roof, or dome, *i*, and equidistant from the piers, *e*, *e*, is a rectangular opening, *o*, on each side of which, resting on the dome, is a little vertical wall, *p*; these side walls, *p*, are connected at *q* by a transverse wall sloping forwards and outwards. Across *o* is placed a large flat quarry, *r*. A flue is thus formed as indicated by the arrow; it may be closed more or less by moving the brick, *s*, forwards or backwards. The

space in front of *o* from the top of the arch *h* to the arch above; *m*, is built up as shown at *t*, *t*, *t*, so as to leave a rectangular opening, *y*, above and in front of *o*; through which the pots *β*, *β* may be charged. Leaning against *r*, is a movable slab of fire-brick, *v*, of which the lower end rests on a ledge formed in the upper part of the arch *h*, at *x*; this slab is bevelled off towards each end, so that flame may issue freely from the opening *o*, both behind and in front of *r*, and escape upwards through the cone. The brickwork above the upper end of the opening *y*, is supported by the bar of iron *w*. The construction between the other piers, except those contiguous to the ends of the fire-place, is the same; so that in all there are six similar openings, *o*, in the dome, *i*, one above and in front of each pot. The piers are firmly supported by cast-iron standards, *δ*, *δ*, which fit on the angles; at the bottom they pass into the brick-floor, and above they are fastened by wrought-iron tie-rods, one of which connects each opposite pair of standards; these rods are purposely omitted in the wood-cut, in order to avoid confusion. The bricks forming the arches, *h*, are also omitted in the sectional elevation for the same reason. It is hardly necessary to observe that only those parts of the furnace which are exposed to a high temperature need be built of fire-brick.

Mode of making the pots.—They are made by the furnace-men. The material used consists of the following mixture: *best* Stourbridge clay, 7 cwt.; *seconds*, 5 cwt.; glass-house pots-herds, 3 cwt.; and old spelter-pots, 6 cwt.; making a total of 21 cwt., which suffice for three pots. The pieces of old pots are freed from vitreous or other matter on the surface, and then reduced to coarse powder. The mixture is kneaded with water to the proper degree of consistency. The pots are formed in a mould, which is merely a strong wooden barrel without top or bottom: it is shown in fig. 126. It is made to separate into three equal segments, the staves of each segment being fastened together at their ends by segments of flat iron. Where two segments join, as in the course of the vertical dark line in the centre of fig. 126, two pegs, *a*, *a*, project from the edge of one and fit into holes in the edge of the other. The barrel is bound by two hoops of iron, of which the lower or smaller one is made to open, as it is not wide enough to be slipped over the upper part of the finished pot after the removal of the segments of the barrel; the ends of this hoop are united by a staple and wedge. The pot is moulded *gradually*, day after day, by hand from the bottom upwards round the inside of the barrel, wooden mallets and other suitable instruments also being used for the purpose. The bottom is beaten down with a wooden rammer. In order to form the top, the apparatus in fig. 127 is employed. It consists of an

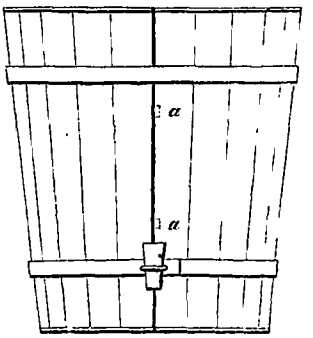

Fig. 126.

upright rectangular stem of wood, *a*, about $2\frac{1}{8} \times 1\frac{1}{4}$ inch, fixed in a wooden foot. On this stem slides a disc of wood, *b*, bevelled at the circumference, as shown in the figure. A ledge is thus made, on which rest the narrow ends, *d*, of a series of pieces of wood, *e*, extending all round: the broad ends of these pieces rest on the upper edge of the pot. The piece *b* is supported by iron clasps, *c*, *c*: there is a row of holes one above another in the upper part of the stem to receive the clasps, so that *b* may be fixed higher or lower, according to circumstances. The upper part of the pot is then moulded upon the sloping roof formed by the pieces of wood, *e*. The clasps are afterwards loosened, when the disc *b* drops, and the pieces of wood, *e*, are removed. The hole in the middle is evenly rounded by means of a round piece of wood. The barrel is now taken away, and the pot allowed to dry gradually. A stock of pots should always be kept in a dry and warm place near the reduction house; they should not be used too soon after they are made. The value of a pot is about twenty-five shillings. When the furnace is cold, and new pots are to be set, each pot is laid on its side in a segment of the barrel, as in a cradle, and drawn to the furnace. A hole, 7 inches in diameter, is drilled in the bottom, by a drill formed like a trident. The external surface of the pot is coated with river mud, which by the action of heat produces a glaze. The mud is taken from a river in which the tide rises high, so that it doubtless contained salt, which would tend to vitrify the surface of the pot.

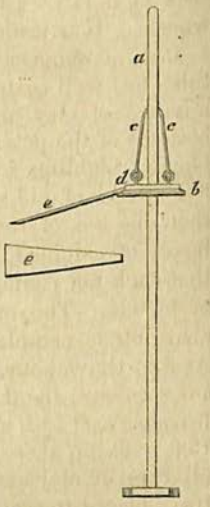

Fig. 127.

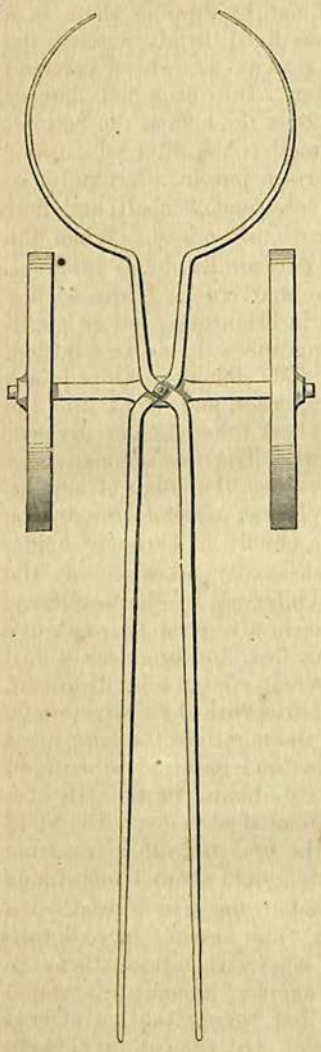
Fig. 128.

The pots are then fixed in position, a little powder of burnt pot having been first strewn on the bed on which they stand. The walls, γ, γ, fig. 125, are now built up, and the furnace is gradually heated. When it is in working order, and a cracked or corroded pot is to be

replaced by a new one, the latter must be first gradually heated to redness in a kiln constructed for the purpose, and while red-hot wheeled into the furnace by means of the instrument, fig. 128: it consists of a large pair of tongs, by which the pot is grasped, set on wheels. It is made wholly of iron.

Mode of charging the pots, and management of the furnace.—The short tubes are well coated with clay, inside and out, by dipping them in a mixture of clay and water; they are then fixed firmly against the bottoms of the pots. The charge for six pots is 20 cwt. of calcined blende, yielding from 6 to 8 cwt. of spelter. Into each pot four or five pieces of old wood, or *plugs*, are put over the hole at the bottom, then one box of rough coke and one of small coke; after which four boxes of calcined blende and four of coke are put in alternately, so that each pot contains six boxes of rough coke, one of small, and four of blende. The ore and coke are not previously mixed. When the charging is completed, the covers of the pots are fixed and luted on. At first the vapour, which escapes from the short tubes, burns with a *brown* colour; the flame gradually increases in brightness, and at length becomes *light blue*, an indication that the long tubes should be adjusted. Before fixing these, their upper or narrow ends should be dipped in a mixture of clay and water. The zinc condenses, and drops into the trays placed to receive it. Occasionally a short tube becomes stopped, especially at the junction with the long one. The furnace-man then detaches the long one, and endeavours to extract the lump of zinc by tongs. If he fails in this, he applies a piece of red-hot iron to the metal and melts it. The gas, consisting chiefly of carbonic oxide, with a little vapour of zinc, which occasionally takes fire at the mouth of the long tube, is extinguished at intervals by the workman; it may then, by admixture with atmospheric air, form an explosive compound, which from time to time catches fire, and produces a dull sound, reverberating through the *cave*. When a long tube drops off, the vapour at the mouth of the short tube burns with the characteristic flame of zinc; but generally the flame at the mouth of the long tubes is blue, like that of carbonic oxide. The time required to work off one charge of 20 cwt. of calcined blende is 67 hours, or the $\frac{1}{4}$th of a fortnight. The average yield may be estimated at 8 cwt.; the yield will necessarily vary with the quality of the ore, and other incidents of the process. One furnace will, therefore, yield about 1 ton of zinc in a week. A mixture of binding and free-burning coal is used, with a clinker-bed, just as in the copper-works. The amount of coal consumed at the Morriston Works per ton of zinc varied from 22 to 27 tons; and at the Mines-Royal Works the average amount was stated to be 24 tons. It is important to note that the proportion of coal does not vary with the richness of the ore. On the contrary, experienced furnace-men assured me very positively that a poor ore requires *more* coal for its reduction than an equal weight of rich ore. Three furnace-men are required for each furnace. During the entire process the fire must be well attended to, and the heat gradually increased. The pots should be frequently examined, and

any leakage must be stopped by the application of fire-clay: neglect in this respect may cause great loss of spelter. When the zinc ceases altogether, or only falls in drops now and then from the long tubes, it is a sign that the charge requires to be renewed; for the ore which may still remain in the pots unreduced cannot be further treated with profit. The stoppers, or covers, must now be removed from the tops of the pots, and the tubes detached. The residuum must be extracted through the holes at the bottom of the pots, of which the inner surfaces must be carefully freed from adherent matter by means of iron tools introduced from above and below. This done, the process is repeated as before.

Treatment of the rough zinc.—The metal as at first obtained is in lumps, formed by the agglutination of the particles of zinc which drop from the tubes. Sometimes stalagmites, as it were, a foot or two in length, are thus produced. In this state the metal is called *rough zinc*. It is melted in cast-iron pots, well stirred, and skimmed all the time; it is then laded into flat open moulds of iron to form ingots, or cakes, of the usual size and shape. The skimmings are called *sweeps*; they contain much metallic zinc, and are worked over again with the ore.

Cost of production.—In 1859 and the 2 years preceding, it varied from 12*l.* to 14*l.* per ton. In 3 years 692 tons of zinc were made, when the average annual cost of *coal* was 7*l.*,—*wages* 5*l.* 5*s.*,—and *materials* (clay, bricks, &c.) 1*l.*,—or a total of 13*l.* 5*s.* per ton of zinc. To this must be added the cost of *blende*, of which about 3 tons were required per ton of zinc, at prices ranging from 2*l.* 15*s.* to 3*l.* 5*s.* per ton. The actual cost, therefore, of the ton of zinc was not less than about 22*l.*

SILESIAN PROCESS OF EXTRACTING ZINC.

In this process the reduction is effected in large retorts, and the distillation is *per ascensum*: the vapour of the zinc being conducted from the *upper* part of the mouth of each retort downwards through a suitable arrangement of condensing tubes.

I am indebted to Mr. William Penrose, of Swansea, for the following information concerning the process which is conducted at Messrs. Dillwyn and Co.'s works at Llansamlet, near Swansea, which are under his management. An argentiferous blende is treated at these works, chiefly for the sake of the silver.

Retorts and appendages.—The form and dimensions of the retort are given in the annexed engravings, fig. 129 (1, 2, 3); its walls gradually increase in thickness towards the back, or closed end, which is nearest the fire-place. On each side of the mouth within is a small projection, or bridge-piece, *v*, *v*. The retorts are made of a mixture of about equal weights of the best Stourbridge clay in a finely divided state, and the powder of old glass-pots, or potsherds: the potsherds are broken up, and the pieces, from which adherent vitreous matter has been chipped off, are crushed between rolls; the ground stuff is sifted

in a sieve of 20 holes to the square inch, and the powder which passes through is employed. The mixture of clay and powder of

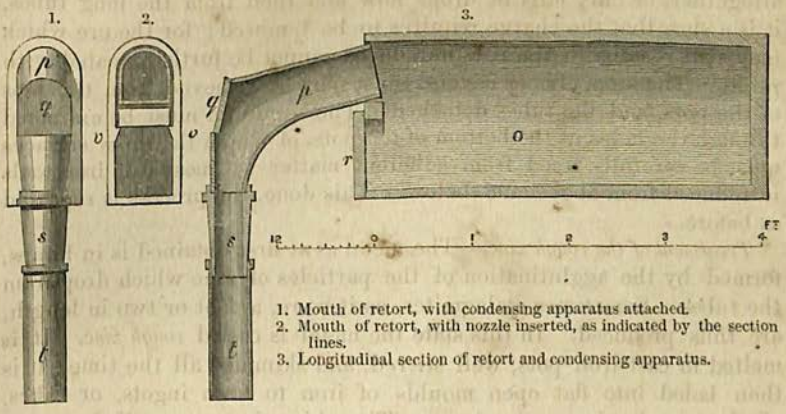

Fig. 129.

potsherds is suitably moistened with water, and well tempered by working it during several hours with a heavy piece of wood; after this treatment it is allowed to stand for a few days. The mould and tools used in making the retorts are represented in the annexed engravings (fig. 130). The mould is made of wood clamped with iron straps, and is in two equal and similar lengths. Fig. A 1 is a side elevation of the entire mould, and fig. A 2 an elevation of the same, corresponding to the flat side or bottom of the retort; the line of junction of the two lengths is shown by the three transverse lines nearly opposite the Nos. 1, 2, fig. A: A 3 represents the top of the lower length, the bottom of which rests on a rectangular board, termed the base-board; it is faced with iron, upon which are seen four projecting pieces, or snugs, which enter into corresponding holes on the lower end of the upper length. Each length is divided vertically into two equal parts across the long transverse axis: see figs. A 2, 3; and these parts are also fitted with snugs on the central vertical line of junction, fig. A 2. The two parts forming each length of the mould are securely fastened together by iron straps and screws, as is sufficiently shown in the engravings. Figs. C, D, E, F, represent various wooden implements used in moulding the clay mixture, which, for the sake of brevity, will hereafter be termed simply clay. The retorts are made in the following manner:—The lower length of the mould is placed vertically on the base-board with the iron straps adjusted, as shown in fig. A 3. The interior of the mould and the base-board are wetted, and dusted over with ground fire-brick to prevent adhesion. A lump of clay is put in, and well beaten down over the bottom with the stamper, C. The sides are roughly formed by hand in successive courses, or small layers, by kneading with the hand rolls of clay, about 6 in. long and 1½ in. in diameter, round the interior of the mould from the bottom upwards. When the coating of clay reaches the top of

the mould, its internal surface is smoothed off by means of the wooden tools D, E, F. The upper length of the mould is then fitted on the lower length, and coated with clay in a similar manner. On the little model, B, a piece of clay is moulded, which, when cut in two, forms the bridge-pieces, which are correctly fixed in the mouth of the retort by the use of a small notched stick as a gauge. In the course of three days the mould may be removed, and the retort standing on the base-board put aside to dry during three months, after which it will be ready for use. When dry a retort weighs about 1¾ cwt. Before they are set in a furnace already in work, they are gradually heated to a strong red heat in a kiln or annealing-oven.

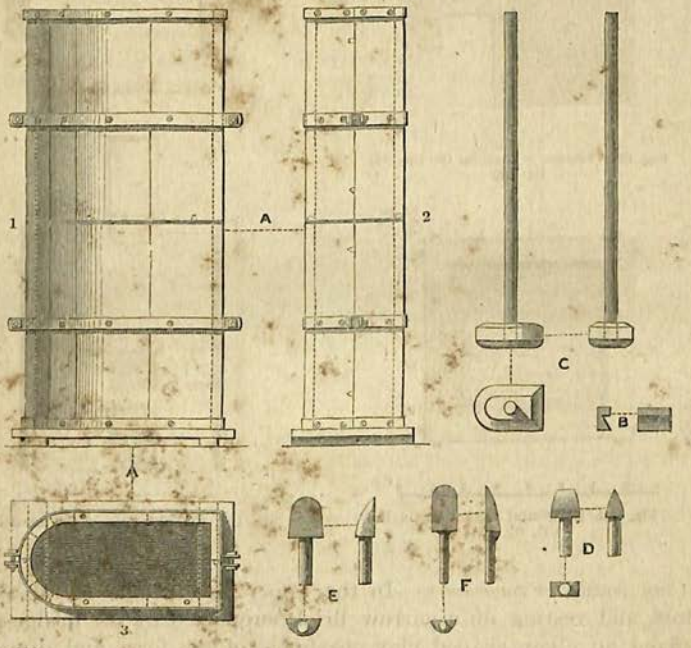

Fig. 130.

Annealing-oven.—The construction of this oven, or kiln, will be clearly understood from the annexed engravings. Fig. 131, vertical section on the line A, B, fig. 132; fig. 132, horizontal section on the line C, D, fig. 131; fig. 133, front elevation; fig. 134, end elevation, in which is the fire-door. The fire-place is arched over; and in the arch are 12 rectangular openings into an arched chamber above, in which the retorts are heated, and which may be termed the retort-chamber. In fig. 131, the draughtsman, in order to make the construction more evident, has taken a liberty, and shown openings actually in this part of the roof of the fire-place, whereas they should have only been indicated by dotted lines. In front, the retort-chamber is closed by an iron door lined on the inside with fire-brick, and suspended and counterpoised as shown in figs. 131, 133. With proper care and under ordinary circum-

stances a retort will last seven weeks in the hottest part of the furnace, and from 10 to 12 weeks in other parts.

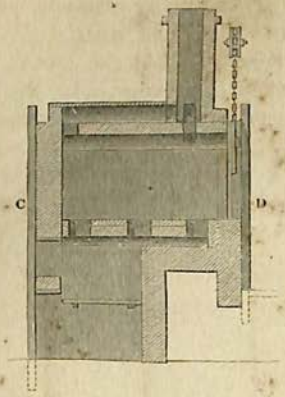

Fig. 131. Vertical section on the line AB, fig. 132.

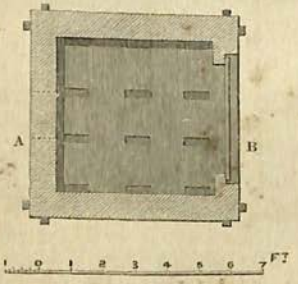

Fig. 132. Horizontal section on the line CD, fig. 131.

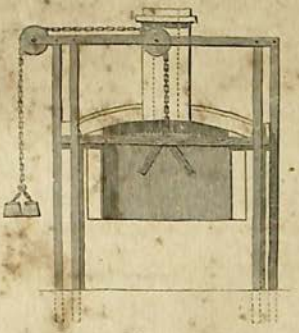

Fig. 133. Front elevation.

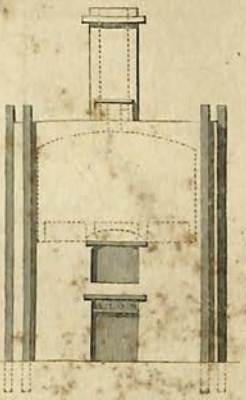

Fig. 134. End elevation at the fire-door.

Clay nozzles or condensers.—In the upper part of the mouth of each retort, and resting on a narrow brick supported by the bridge-pieces, is fixed an elbow-shaped clay nozzle, *p*, of the form and dimensions shown in fig. 129 (1, 3). There is an opening, *q*, at the elbow; it is closed with a flat piece of clay, luted on, which may easily be knocked off when necessary. They are made of a mixture of 2 parts, by measure, of ground fire-brick and 1 part of pipe clay, duly mixed with water and tempered. They are formed in a plaster of Paris mould, consisting of two equal and similar parts, one of which is shown in H, fig. 135: it presents a concavity and flat borders, on which are conical depressions, which fit into corresponding projections on the other half of the mould. The ends of the mould, when the halves are united, are shown in H, 1, 2, respectively. The nozzles are formed in the mould by hand, a wet sponge and small iron scraper only being required. The clay is kneaded carefully over the concave surface of each half of the mould; the halves are then put together, and the workman introduces his hand and unites the edges of the clay

solidly together along the line of junction. Moulds are made on a plaster of Paris model, which consists of one concave piece in plaster of Paris and a wooden core or block, G, fig. 135. It is obvious that with such a model both halves of the mould may easily be made.

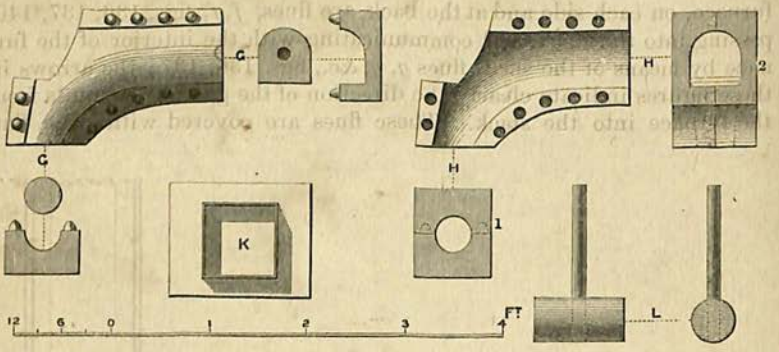

Fig. 135.

Laggins or stoppers.—The mouth of the retort below the nozzle is closed with a flat piece of clay, which is made by merely beating clay into a movable square iron frame K, resting on a cast-iron plate, with the wooden mallet, L. The iron of which this frame is made is $\frac{7}{16}$ in. wide by $\frac{3}{4}$ in. deep.

Iron appendages.—On the lower end of the clay nozzle is fitted a short somewhat conical cast-iron tube, having a flange at the upper or widest end, *s*, fig. 129 (1, 3), and over the lower end of this cast-iron tube is fixed a sheet-iron tube, *t*, fig. 129 (1, 3). The cast-iron tube *s* is supported in its position on one side by the flange which rests on the cast-iron plate *l*, fig. 138, and on the other by an iron wedge.

Description of the furnace.—The bed of the furnace on which the retorts rest is flat, horizontal, and rectangular. It is bounded on each side by six equal and similar arched recesses, *i*, *i*, figs. 136, 140; in front by a vertical wall in which is the fire-hole, *d*, fig. 137; at the back by a similar wall, behind and contiguous to which is the stack; and above by an arch, *k*, fig. 140, extending from side to side. Below the fire-place is an arched passage, *b*, figs. 137, 140, through which air is supplied to the fire, and the stoker can get access to the grate. The sides of the opening in the arch below the grate are formed of iron plates, *c*, fig. 137, which are kept in their place by three transverse bars of iron, figs. 137, 140. The vertical partition-walls, *h*, *h*, fig. 138, of the arched recesses are made of single large fire bricks, upon which are other fire-bricks, fashioned so as to form suitable abutments for the arches, as indicated in fig. 136. Below the arched recesses is a corresponding series of rectangular niches *a*, *a*, figs. 136, 140, of which the bottom is level with the floor of the reduction house. The niches are only partially covered at the top by the cast-iron plate, *l*, *l*, fig. 138, which rests on

the vertical brick walls forming the sides of the niches, fig. 136; narrow spaces are thus left open above at the back, *a*, *a*, fig. 138. In the roof of the furnace are three rectangular openings, *e*, *e*, *e*, figs. 137, 140, which are closed by movable fire-bricks or slabs. At the top of the furnace, on each side and at the back, are flues, *f*, *f*, figs. 136, 137, 140, passing into the stack, and communicating with the interior of the furnace by means of the small flues *g*, *g*, &c., figs. 136, 137; the arrows in these figures indicate clearly the direction of the gaseous currents from the furnace into the stack. These flues are covered with large, flat,

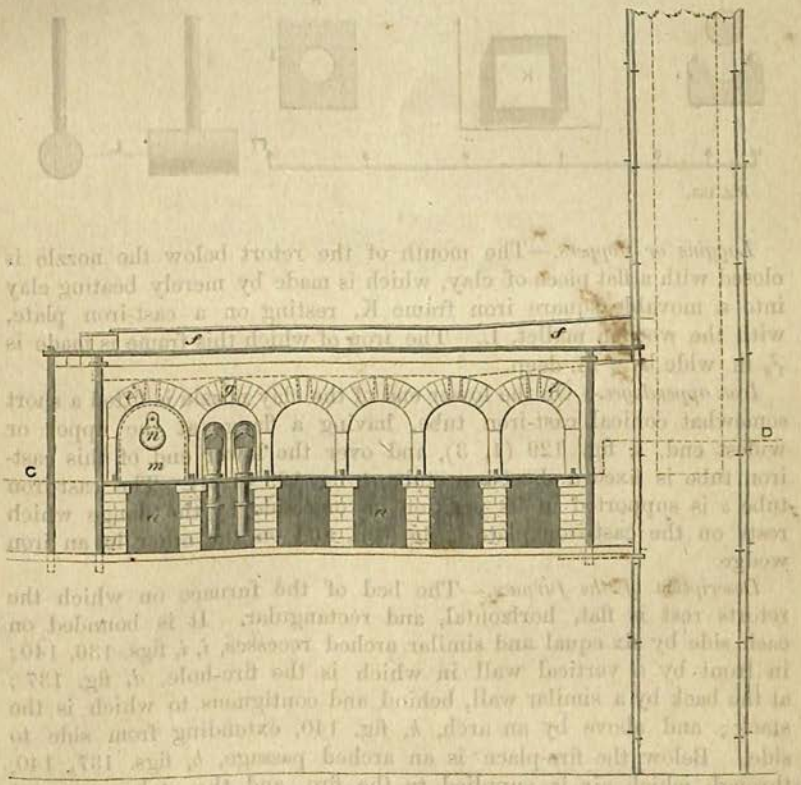

Fig. 136. Side elevation.

movable fire-bricks or slabs. In the front and back walls of the furnace are two openings, which communicate directly with the interior, and also with the flues at the top; they are made to facilitate the cleaning of the upper lateral flues. The object of this arrangement of flues is to produce as equable a temperature as possible in every part of the furnace. The furnace is strongly braced by means of iron standards and tie-rods, as is sufficiently indicated in the engravings. In each arched recess two retorts are placed, as shown in one of the recesses in fig. 138. The open space round their mouths is carefully

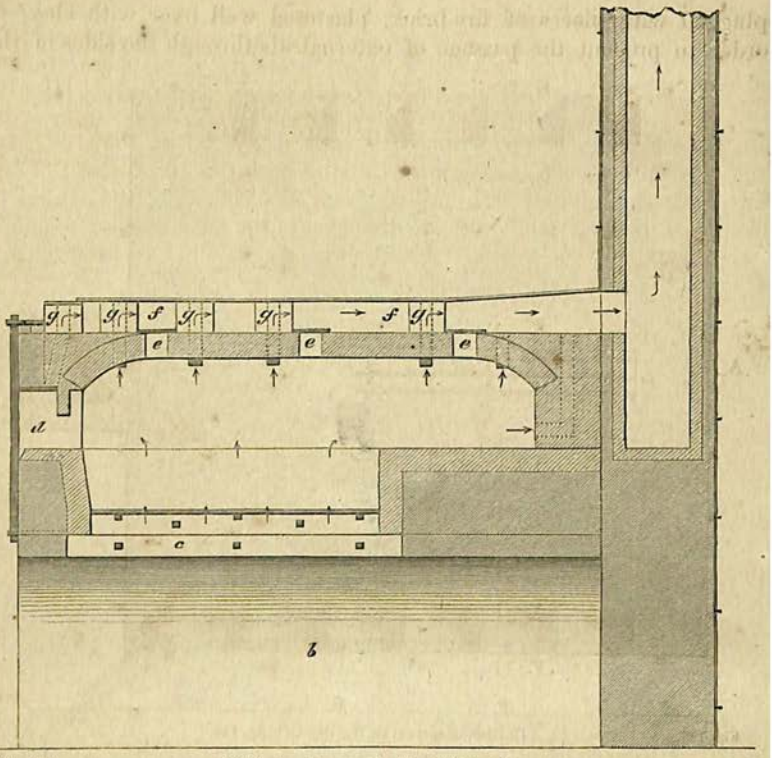

Fig. 137. Vertical section on the line AB, fig. 139.

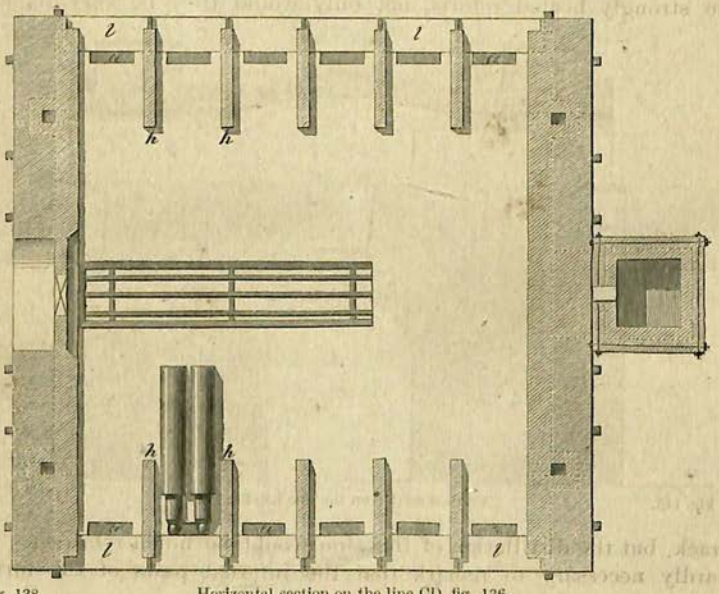

Fig. 138. Horizontal section on the line CD, fig. 136.

plugged with pieces of fire-brick, plastered well over with clay, in order to prevent the passage of external air through the sides of the

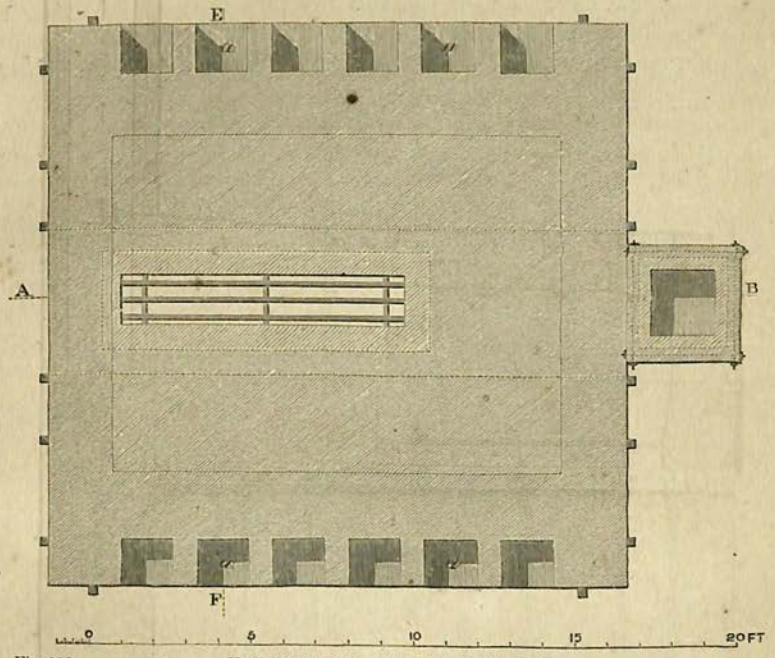

Fig. 139. Horizontal section on the line GH, fig. 140.

furnace into the interior; for, if cold air were allowed to impinge upon the strongly heated retorts, not only would they be very liable to

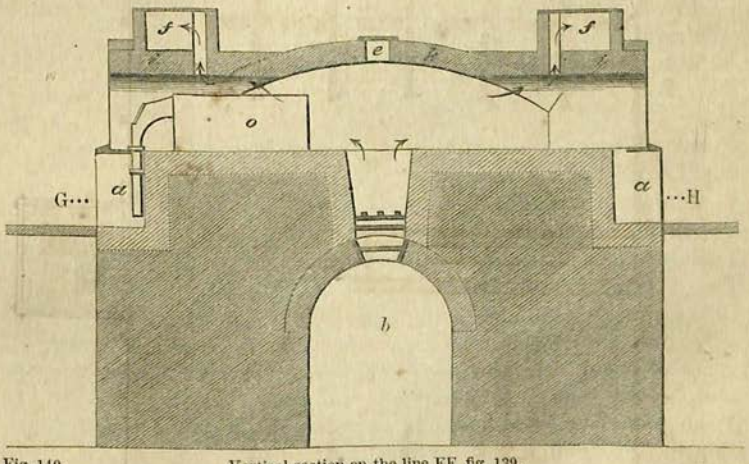

Fig. 140. Vertical section on the line EF, fig. 139.

crack, but the distillation of the zinc would be much retarded. It is hardly necessary to remark that the internal parts of the furnace,

which are exposed to a high degree of heat, are built of fire-brick. The position of a retort with the clay nozzle and iron tubes attached is shown in *o*, fig. 140. During the working of the furnace each recess is closed by a movable sheet-iron door, *m*, fig. 136, in which is a peep-hole, *n*, provided with a sliding cover; by this means the temperature

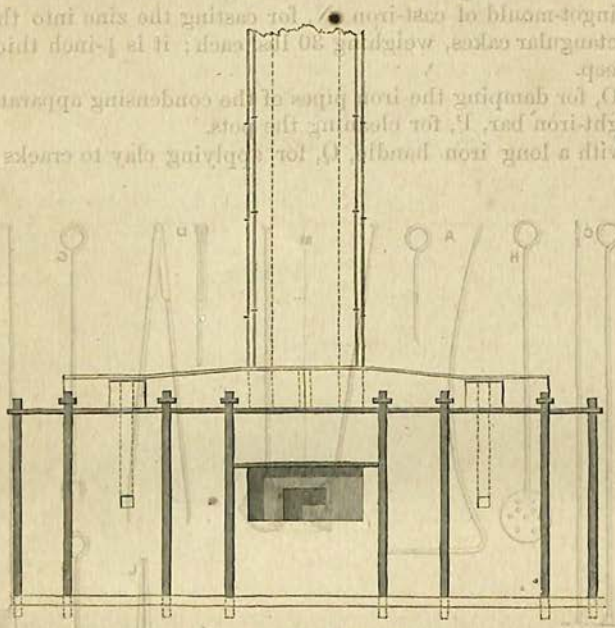

Fig. 141. End elevation at the fire-door.

is kept sufficiently high to prevent the nozzle from becoming obstructed by the solidification of zinc within it. The zinc drops upon the ground or in iron trays, which may be placed underneath to receive it.

Tools employed.—They are represented in the annexed wood-engravings.

Nozzle-cleaners, of wrought-iron, A; one long and one short.

Small mop, B.

Rabble, C, of wrought-iron, 6 feet long.

One ditto, ditto, 5 feet 6 inches long.

Two ditto, ditto, 10 feet long each.

Tongs, D, of wrought-iron.

Charger, E; *a*, side elevation; *b*, end elevation; it is a sort of trough of sheet-iron supported on an iron frame; it is used for holding the mixture of ore during the time of charging, and is moved from one place to another, as convenience may require.

A scoop of sheet-iron, having a long handle, F; it is used for introducing the charge of mixed ore into the retorts.

Door-fork, G, for taking down or putting up the doors in front of the muffles.

Skimmer, H, consisting of a perforated, circular, flat plate of iron,

with a wrought-iron handle; it is employed in skimming the zinc in the process of remelting.

Skimming-box of sheet-iron, K, for receiving the skimmings.

Tongs, L.

Ladle, M, for lading the zinc into the ingot-mould.

Open ingot-mould of cast-iron, N, for casting the zinc into the form of flat rectangular cakes, weighing 30 lbs. each; it is $\frac{1}{2}$-inch thick, and $\frac{3}{4}$-inch deep.

Mop, O, for damping the iron pipes of the condensing apparatus.

Wrought-iron bar, P, for cleaning the pots.

Mop with a long iron handle, Q, for applying clay to cracks in the retorts.

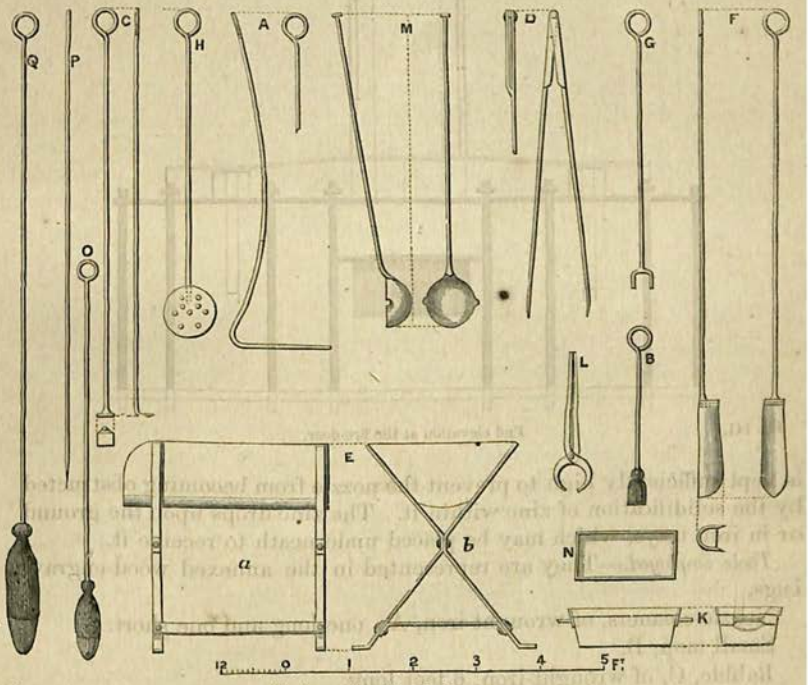

Fig. 142. Tools employed by the furnace-men.

Nature and preparation of the ore.—The ore is blende, or sulphide of zinc, containing sulphide of iron and lead, silver, and a small portion of cadmium. It is ground down under edge-wheels to a fine powder, which is passed through a revolving screen containing 225 holes to the square inch.

Calciner.—The bed of the calciner consists of two floors, or rather of one floor divided into two parts; that which is nearest the flue and furthest from the fire is 15 feet long and 5 inches higher than the other, which is 12 feet long. The width of the bed is 9 feet through its entire length. The height of the fire-bridge is 2 feet 4 inches.

The roof in the centre is 3 feet 4 inches above the lowest floor, but it gradually inclines downwards, so that, at the extreme end of the calciner, it is only one foot above the floor. Air enters the furnace through holes in the fire-bridge as well as through other parts. Above the roof, and over the highest floor, are two bins or hoppers, large at the top, and about 6 inches square at the bottom. Each is capable of holding half a ton of ore. Immediately below each hopper is a hole in the roof, through which the ore falls into the furnace. There is only a small slab between the bottom of a hopper and the corresponding hole in the roof underneath. The charge consists of one ton of blende, which is spread over the entire surface of the highest floor, and is carefully stirred every ten minutes. The temperature gradually rises to dull redness from the simple oxidation of the blende. At the eleventh hour the ore is drawn down to the lowest floor, and its place is immediately supplied by a fresh charge, similar to the first. The first charge having been calcined during 11 hours, it is further calcined during 11 hours at a temperature gradually raised from dull to bright redness, during which time it is most carefully stirred. When sulphureous vapours cease to be evolved, the calcined ore is allowed to fall through an opening in the bed of the calciner leading to a vault underneath, where it cools. Another charge is immediately drawn down from the first floor, and the process repeated in the manner just described, so that a fresh charge of calcined blende is drawn at intervals of 11 hours.

In order accurately to ascertain the results of the calcination, every charge of ore was carefully weighed in and out of the calciner for one month continuously, and the whole was afterwards carefully worked through the distilling furnace. The products were again accurately noted. The loss by weight in calcination, on an average of 32 days, amounted to $19\frac{1}{16}$ per cent. The blende in its raw condition yielded by careful assay 37 per cent. of zinc, and after calcination 43·4 per cent. This should have been 45·4 per cent., so that a loss of zinc amounting to 2 per cent. must have occurred.

In calcining this blende a portion of the fume disengaged during the operation, as well as some of the finer particles of the ore, was deposited in chambers constructed for that purpose. This deposit consisted of sulphides, sulphates, and oxides of zinc, lead, and iron, &c. At the end of 30 days' work the matters thus deposited were carefully collected and weighed; and when the weight was added to that of the calcined ore stated above, there still remained a deficiency amounting to 1·5 per cent., which was irrecoverably lost.

It is not usual to take so much trouble and to incur so much expense in a process from which such small results are obtained; in fact this could not be profitably done if zinc were the only object of extraction. In order to extract the silver by the method adopted at these works, it is necessary to reduce the ore to a very considerable degree of fineness, and to conduct the process of calcining with extreme care. It has been found by experience that calcination during 22 hours is sufficient to completely oxidize a charge of ore, provided it has received

the proper amount of attention. The calcined ore is desilverized by a special process, and from the residue zinc is extracted. It is the custom in most zinc-works to conduct this operation with the waste heat of the reduction or distilling furnace. This is effected in a calciner having two beds, one over the other, built at the end of the furnace furthest from the fire. The ore is first calcined on the upper bed, which is the least heated, during 12 hours, with occasional stirring, after which it is raked down to the lower bed, where it is subjected to a bright red heat during another 12 hours. At the end of the 24 hours it is drawn out, and is supposed to be ready for distillation.

Distillation of zinc.—The dry charge in the 24 retorts consists of about 1568 lbs. of desilverized calcined blende and about 150 lbs. of sweep or skimmings from the last day's melting; fine bituminous coal 5 cwt., and 2 cwt. of coke or ashes which are collected under the grate: these matters having been carefully mixed, the charge is ready for the retorts. If the charge were equally distributed in the retorts, each retort would receive rather more than 71 lbs. of blende and sweep, exclusive of reducing agents. This, however, is not the case; the retorts nearest the fire-place, being exposed to the strongest heat, are more heavily charged than the others which are further from the fire-place, and which should not receive more of the charge than can be reduced in them in 24 hours. It is usually left to the discretion of the workmen to regulate the distribution of the charge; experience soon teaches them how to proceed so as to obtain the largest amount of zinc from a given charge.

The workmen commence about 6 o'clock in the morning to empty the retorts, which is done in the following manner. The *laggin*, or clay-door, under the bridge, upon which the nozzle rests, is knocked off, when, with the aid of a rabble, the whole contents of the retort are, in a few minutes, drawn out into an iron barrow, which is immediately removed from the building. The clay door in front of the nozzle is also knocked off, and any zinc which may remain on the internal surface of the nozzle is scraped off into the receiver below. Care must be taken to have the retorts thoroughly cleansed, after which they are ready for a fresh charge. The charger, E, fig. 142, being always at hand, with the aid of a scoop, F, fig. 142, the retorts are again filled through the same opening by which they were emptied. Clay doors, previously prepared, are again luted on, both under and in front of the nozzle.

Two workmen are always engaged in emptying and filling the retorts. They proceed in regular order, both men being occupied at the same time with the pair of retorts in one recess. In general between 3 and 4 hours are required to cleanse and charge all the retorts.

Before and during the time of charging, the fire is allowed slightly to cool down; but as soon as all the retorts are filled, the heat is again gradually raised, and at 4 P.M. almost a white heat is obtained. The metal begins to condense in about 5 hours after the retorts are charged, and at 6 P.M. distillation proceeds briskly; this continues until about 3

or 4 A.M. of the following day, when it gradually slackens, and at 6 A.M. it ceases altogether.

The first products that come over are a little moisture, carbonic oxide, and a small quantity of a mixture of oxide and metallic zinc in a finely divided state. This mixture of oxide and metal gradually increases in amount for an hour, after which condensation of zinc slowly proceeds; and, as the nozzles become heated, the metal begins to fall in small drops; the process then goes on until the charge is exhausted.

At the commencement of the distillation a blue flame appears at the lower end of the nozzle, which gradually increases in intensity, and becomes greenish-white; it then as slowly decreases, and finally disappears, when drops of zinc begin to fall, and the process goes on regularly until morning.

The furnace having been charged, and all the leaks having been carefully luted up, one man only takes charge of it and attends to the firing during the night. It is most important that a high and constant temperature should be kept up. The condensers require constant attention: if they become too hot, the metal takes fire and burns, in which case the doors closing the recess in front must be taken down, and not again put up until they are sufficiently cooled; if by chance they should become too cold, the metal would solidify in them and obstruct the passage, when a nozzle-cleaner, *A*, fig. 142, is heated and inserted into the opening, whereby the solidified zinc is speedily melted, and the obstruction removed. This never happens except when the temperature of the furnace is too low, an evil which is generally caused by the choking up of the flue over the retorts.

When any metal is found escaping from the retorts, which is easily known by removing the fire-place door, the workman goes on the top of the furnace, and through one of the holes in the roof he introduces a long iron rod, with a mop at the end, previously dipped in a bucket of fire-clay lute, and mops the spot where the metal is escaping. This has frequently to be done many times during the night, and is most detrimental to the yield of metal, as the frequent opening of the holes in the roof lets in cold air, which cools the retorts and checks distillation sometimes to the extent of 15 per cent. of the metal.

It is also most important that all the flues should be kept open; for if any stoppage takes place, the heat is immediately diverted, and the neighbouring retorts being thus deprived of their proper amount of heat, may not then yield more than half their proper quantity of metal. A diligent workman is always alive to these matters; and as he is paid according to the quantity of zinc produced, he is interested in preserving the proper working of the furnace.

Melting of distilled zinc.—The retorts having been all filled and the doors carefully luted on, the metal from the last charge is now collected together and melted in an iron pot, *a*, fixed over a fire-place: see fig. 143. This pot is capable of holding 8 cwt. of metal. In about half or three-quarters of an hour the whole will be melted, and the face of the metal will be covered with *sweep*, consisting of oxide of zinc in admixture with finely divided metallic zinc; this is removed by means

of the skimmer, H, fig. 142, and must be added to the charge for the retorts on the following day; the metal being thus freed from all impurities except lead, of which it contains from 2 to 3 per cent., and which it is most important should be removed, as otherwise the zinc would be unmarketable. This lead may be separated, though not completely, by the following simple and effective method: the zinc is allowed to remain in the pot during about 20 minutes, and then to cool down almost to the freezing point of zinc, when it is laded into the mould, N, fig. 142; the last ingot will contain the greater part of the lead, and is put aside until a sufficient number of similar ingots has accumulated, when they are remelted, and the melted metal is treated as in the manner just described.

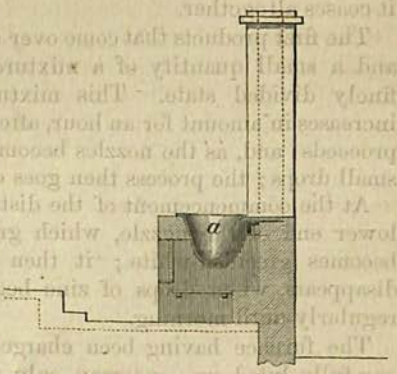

Fig. 143. Vertical section on the line AB, fig. 144.

Yield of zinc.—The charge consists of 1568 lbs. of calcined blende, containing 43·4 per cent. of metal, besides 150 lbs. of *sweep* from the preceding charge, which, in estimating the yield, must not be taken into consideration, as the same quantity of *sweep* is carried on to every successive charge. The same may be said of what the workmen call *pipe-metal*, which is derived from old nozzles: after the removal of an old nozzle, a few pounds of metallic zinc, inclusive of some intermixed oxide, are obtained by breaking them up, and added to the original charge; but as the same deposit is continually renewed, it should not form an item in the present calculation. The average quantity of metal produced after 30 days' work amounted to 566 lbs. each day: 1568 lbs. of calcined blende, at a produce of 43·4 per cent., should give 680½ lbs., so that there is a loss on the calcined blende of 7·4 per cent.,—that is, only 36·4 per cent. of zinc is obtained instead of 43·4 per cent. The loss in calcination was 1½ per cent., which, added to the above, viz., 7·4 per cent., leaves a total deficiency of nearly 9 per cent. The greater part of this loss is to be accounted for by the zinc in the residues, and is chiefly owing to the unequal distribution of heat over the retorts. In emptying the retorts, it is noticed that the first portion removed is still rich in metal; and this is from the coldest part of the retort, and close upon the nozzle. Further in, the residue becomes poorer and poorer, until at the furthest end, where the heat is greatest, it is found that the blende has been entirely exhausted of its metal.

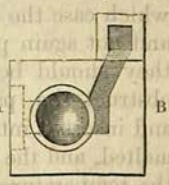

Fig. 144.

Consumption of fuel.—The quantity of coal used in 24 hours is as follows:—

	Ton.	cwt.	qr.
Free-burning coal	1	4	2
Bituminous	1	8	0
Coal mixed with the charge	0	5	0
Total	2	17	2

or as nearly as possible 11½ tons to 1 ton of zinc. In all cases where rich blendes and calamines are treated in admixture with sweep, a less quantity of coal will produce a much larger quantity of metal. The richer the ore, the lower the temperature required for distillation; and the greater the produce, the less there is to pay per cwt. for workmen's wages. In these works 2*s.* 8*d.* per cwt. is paid in wages; whereas, if 10 cwt. of zinc were produced instead of 5 cwt., 1*s.* 4*d.* would be the charge on the metal instead of 2*s.* 8*d.* It is therefore quite manifest that the richer the ore the more cheaply can the metal be extracted.

Repairs.—A zinc furnace works continuously during 13 months, at the end of which time it becomes necessary to let the fire out for repairs. In this case the retorts are all broken up, and replaced by new ones. In the first charging they receive only a small quantity of blende, and the metal from this is all absorbed by the substance of the new retorts; by the seventh day they receive their full charge, and it is not till then that they yield their proper quantity of metal. A furnace with proper care will last four years. It must then be taken down as far as the grate, and rebuilt.

Modifications of Details of the Process.

Retorts.[7]—In Silesia they are made without moulds, and it is stated that they are preferable to those made in moulds; because in the latter, the clay being unequally built up, a very large number of minute imperceptible cavities may exist by which zinc would escape, and the successive courses of clay do not well unite with each other. It has been remarked that in the Silesian furnaces in Belgium, the retorts which are made in moulds generally crack along the lines corresponding to the joints of the mould. But I do not understand why these defects should occur in retorts made with proper care in moulds such as I have described. The retort-maker begins by forming a solid prism of the clay of the size of the closed end of the retort. He hollows out this in the interior, taking care to leave a tolerably thick border, which he afterwards reduces by hand. He then forms a plate of clay by strongly beating it, cuts it so that it will extend about half round the retort and about 8 inches upwards, and carries it on his chest to the part already fashioned. He carefully unites the edges which come in contact, having previously made them uneven in order to ensure a better union. This done, he adds another similar plate of clay so as to complete this portion of the retort, and then leaves the whole to dry during several days, taking care to keep the upper edges moist by covering them with a wet cloth. Without this partial desiccation the moulded portion would be too soft to sustain any additional weight of clay. The retort is thus built up at intervals, and it receives

[7] The following information is chiefly derived from the "Mémoire sur la Métallurgie du Zinc dans la Haute-Silésie (Prusse). Par M. Julien, ingénieur des mines." Ann. des Mines, 1859, 5. s. 16, pp. 477-528.

a finish by holding a flat board (of the height of the retort and about 4 inches broad) against the outside, and beating the corresponding surface of the interior with a small wooden mallet; every part is thus treated in succession, a broad flat board being used against the bottom, which should be made very level. It is stated that a retort will be ready for use in about 15 days after completion. The method of manufacturing retorts above described is the same as that adopted in the manufacture of glass pots.

All the furnaces in Silesia are built in pairs. The platform on which the retorts rest inclines slightly from the fire-place. Attempts have been made from time to time to improve the Silesian method; but it would appear that no better results have been obtained than those yielded by the furnaces containing 20 retorts, which were in operation 20 years ago. It was expected that by constructing furnaces to hold a larger number of retorts, fuel would be economized; but the reverse of this expectation has been found by experiment. Furnaces containing 24, 26, 28, and even 30 retorts have been tried, and in all the consumption of fuel has been greater than in the furnaces holding 20 retorts. The following average results have been obtained during a month's working:—

Number of retorts in a furnace.	Quantity of ore treated (calamine).	Fuel (non-caking coal) consumed.	Zinc obtained.	Coal consumed per quintal of zinc.	Yield of zinc per cent.
20	53·55	138·70	10·30	13·42	19·23
24	60·70	152·00	10·85	14·00	17·49
30	67·83	178·60	11·48	15·55	16·89

The weights are in metrical quintals (q. m.): 1 met. q. = 100 kilogrammes, or nearly 2 cwt.

Attempts have been made to apply heat directly to the bottoms of the retorts by supporting them on bricks, so that the flame might play under them; but rapid destruction occurred at the angles formed by the lower and posterior faces.[8]

The *crude*, or *rough*, zinc is now melted in clay vessels, cautiously heated, in order to avoid contact with iron, which is readily acted upon by melted zinc, and the presence of which in zinc greatly deteriorates its quality for rolling.

At Stolberg in Saxony, where the Silesian process is carried on, the condensing apparatus consists of a clay receiver about 2 ft. long, and of the form shown in the annexed wood-cut. It is fixed in the upper part of the retort like the elbow-tube above described. The metal collects in the lower or bellied-out part, from which it is laded at intervals. On the free end a sheet-iron vessel is placed, somewhat similar to that hereafter to be described under the head of

[8] Mémoire sur l'exploitation de la calamine et la fabrication du zinc dans la Haute-Silésie. Par M. Callon. Ann. d. Mines, 1840, 3. s. 17, p. 71.

the Belgian process; but the use of this, I am informed, has been discarded, at least in some works.

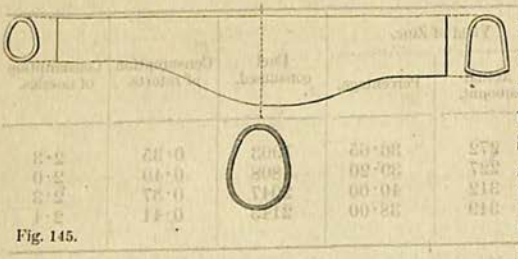

Fig. 145.

The results which Julien has recorded of the working of large furnaces containing more than 20 or 24 retorts in Silesia, are, as we have seen, unfavourable, at least with respect to the consumption of fuel. But these results are opposed to the experience obtained at the Vieille Montagne Company's Works, where furnaces containing 24, 28, 32, and even 40 retorts have been in operation. The furnaces of the most approved construction differ from that of which I have given illustrations, and from those described by Julien at the Government and the Silesian Company's Works. There are flues *under*, but *not over*, the retorts, for the escape of flame from the furnace. A flue extends under each row of retorts at some distance below them, and its outer side is immediately under their mouths. There are thus two flues which are arched, and are constructed in the solid brickwork between the sides of the fireplace and those of the furnace; they communicate with the stack. Just behind each partition-wall (see fig. 138, *h*, *h*) is an opening, and another on the same line between each pair of retorts; and all these openings pass directly into the flues running underneath. This arrangement is stated to be much superior to the old one with flues over the retorts. The retorts are more strongly heated at the bottom, where heat is required, and not, as in the old ones, at the top, where it is unnecessary. The closed ends of the retorts extend to the sides of the fireplace. Each recess contains a pair of retorts. The reason assigned for making the beds supporting the retorts to incline slightly *from* the fireplace is, that any slag produced in the retorts may flow forward towards the coolest part, and not remain in contact with the back or hottest part, where it would prove highly corrosive. Moreover, another reason alleged for the inclination is, that the inner part of the bed of the furnace being exposed to the greatest degree of heat, is apt to sink more than the outer, so that if the retorts were originally placed horizontal, they might after a time become inclined towards the fireplace; and it is stated that this inclination would be very injurious in more than one respect. In front of the muffles are openings communicating with passages under the floor, and these again communicate with the exterior. The residues from the retorts are allowed to fall through the openings in question, and may be taken away without in any degree incommoding the furnace-men.

It is estimated that a Silesian furnace lasts on an average 2 years, with a monthly consumption of 8 retorts.

In the following table by Thum are given the average daily charges,

consumption of fuel, &c., of the Silesian furnace at one of the Vieille Montagne Company's Works:—

No.	Charge.		Yield of Zinc.		Fuel consumed.	Consumption of retorts.	Consumption of nozzles.
	Calamine.	Coal for reduction.	Actual amount.	Percentage.			
	kil.	kil.					
1	686	175	272	36·65	1903	0·35	2·3
2	580	150	227	39·20	1808	0·40	2·0
3	780	200	312	40·00	2047	0·37	2·3
4	920	230	349	38·00	2143	0·41	2·4

No. 1. Daily average per furnace in July, 1857.
No. 2. ditto ditto with 24 retorts.
No. 3. ditto ditto ,, 32 *small* retorts.
No. 4. ditto ditto ,, 32 *large* retorts.

The coal consumed as *fuel* per ton of zinc is as follows:—No. (1), 6·99; No. (2), 7·96; No. (3), 6·56; No. (4), 6·14.

These results, so far as relates to the consumption of fuel, are in favour of the large furnaces. The cost of labour also is proportionately less in the large furnaces. Thus the average cost of labour in extracting 100 kil. of zinc was as follows:—No. (2), 4·98 francs; No. (3), 3·62; No. 4, 3·24.

The average cost of extracting 100 kil. of zinc was as under:—

	Francs.
Labour	4·16
Coal (at 9·60 francs per 1000 kil.)	7·33
Retorts	0·62
Various refractory materials	0·50
Cast- and wrought-iron	0·05
	12·66

Estimating 1000 kil. = 1 ton, the average cost per ton of zinc is 5*l.* 5*s.* 6*d.*

Cost of Production.

The following information on the cost of production in Silesia is extracted from Julien's Memoir, already referred to:—

The furnace-men are always paid according to the quantity of zinc produced. The rate of wages varies with the produce of the ore; and it is so arranged that on the average the head furnace-man receives 1*s.* 10*d.*, and his assistants 1*s.* 6*d.* per day each. The labourers employed in porterage in the works, and in attending to the fires, receive 1*s.* ½*d.* per day each. There are three furnace-men to each furnace—one head man and two assistants. The retort-makers receive 9*d.* for each retort when they mix the clay themselves, but otherwise only 6*d.*

The charge for each furnace in about 24 hours is from 7 to 8 quintals (from about 14 to 16 cwt.), and the yield of zinc is from 1·06 to 1·16 (about 2 cwt.), that is from 15 to 16 per cent. The yield, with a given

ore, depends in great measure upon the furnace-man, but it also depends upon the furnace: thus an old furnace always produces less than one which has been at work for some time. The average cost of the different kinds of calamine treated is 1*s.* 3*d.* the quintal at the mine, and carriage costs about $3\frac{3}{10}d.$

The consumption of fuel in 1857 was not less than 20 quintals for 1 of the zinc produced, or double what it was in 1838. This is explained by the fact that the ores have become much poorer, the ratio of the produce in the years above-mentioned being respectively as 2 : 5.

The price of coal is from about 5*s.* to 5*s.* 10*d.* per ton.

For every ton of zinc produced, the proportion of retorts requiring to be replaced is $3\frac{1}{2}$; and the proportion of clay vessels for remelting the zinc is about 10 times less. A retort costs about 4*s.* 7*d.*, and a remelting vessel 5*s.* 2*d.* It is estimated that on an average a pair of furnaces, at least those newly constructed, cost 120*l.*, and the corresponding part of the edifice 160*l.* At the Lydognia Works, and generally in all the old works, the cost is considerably less.

At the Lydognia Works, which belong to and are carried on by the Prussian Government, 8950 quintals (about 895 tons) of zinc in ingots were made in 1857, and the expenses were estimated as under :—

	24 francs = £1. Francs.	£.	*s.*	*d.*
Labour	62,645	2610	4	2
Various materials, retorts, re-melting vessels, clay, bricks, bar-iron, pig-iron, repairs of tools, &c.	33,076	1378	3	4
Calamine	240,476	10,019	16	8
Fuel	127,960	5331	13	4
General expenses (interest on capital invested in plant and on floating capital at 5 %)	26,710	1112	18	4
	490,867	20,452	15	10
Hence the cost of production per quintal of zinc is	54·84	2	5	8

This is inclusive of interest at 5 per cent. on a capital estimated at 534,218 francs, or 22,259*l.* 1*s.* 8*d.* The interest is 26,710 francs, or 1112*l.* 18*s.* 4*d.* The actual cost of production, therefore, per quintal, inclusive of the cost of ore, is (20,452*l.* 15*s.* 10*d.* — 1112*l.* 18*s.* 4*d.*) ÷ 8950 = 2*l.* 3*s.* $2\frac{1}{2}d.$; or 21*l.* 19*s.* per ton of 2240 lbs.

This sum is not actually expended in producing a ton of zinc, as the Prussian Government receives by way of royalty $\frac{1}{10}$th of all the calamine raised in Silesia, and the greater part of this is treated at the Lydognia Works. Moreover, the coal consumed is derived from the royal mine called Königsgrube, and its value is estimated at the market price in 1857, which was very high. The calamine, consequently, cost the Government nothing, and the coal considerably less than the amount set down in the account of expenditure.

Julien has published the following commercial details concerning the cost of production, &c., at the private works of the Silesian Company :—

Year.	Production of zinc in metrical quintals.		
	Total production.	Daily production per furnace.	Average yield per cent. from the calamine.
1857	74,707	1·15	14·93
1858 (first half of the year)	41,175	1·11	14·01

Proportion of retorts and melting-vessels to be replaced, per quintal of zinc produced:—

	1857.	1858 (first six months).
Retorts	0·35	0·37
Melting-vessels	0·04	0·05

ESTIMATE OF THE COST OF PRODUCTION PER QUINTAL OF ZINC.

	1857.		1858 (first six months.)	
	Francs.		Francs.	
Labour	6·17		6·15	
Fuel	11·18		12·10	
	francs.		francs.	
Calamine ..... at the mine ...	10·46	12·46	10·43	12·61
Calamine ..... carriage	2·00		2·18	
Refractory matter,—bricks, clay, &c.	1·80		1·83	
Bar-iron, cast-iron, &c.	0·34		0·32	
Repairs	1·36		1·04	
General expenses	1·25		1·31	
Cost of production	34·56		35·36	
Do. per ton	£14 12*s.* 7½*d.*		£14 19*s.* 4¾*d.*	

It is stated that the slight increase of cost in 1858 was caused by diminished produce of the ore.

The difference in the cost of production at the Lydognia Works and those of the Silesian Company is more apparent than real. This Company has its own mines of calamine and coal, and the amount charged for these materials is exactly what was expended in raising them, &c., from the mines; whereas in the account of the cost of production at the Lydognia Works they are charged at their *selling price* at the time. In the latter account, coal is charged at the rate of 7·3 francs per 1000 kilogrammes, while in that of the Silesian Company it is estimated only at 5·61 francs.

In like manner the calamine at the Lydognia Works, though considerably richer, and yielding 16·92 per cent. of zinc, instead of 14·93, is estimated at 26·71 francs per quintal of the zinc produced, or 14·25 francs higher than at the Silesian Company's Works.

By deducting this excess in the price of coal and calamine (3·28 + 14·25 =), 17·53 from 54·84—the cost of production per quintal of zinc at the Lydognia Works—we have the cost of production reduced to 37·31 francs, an amount quite comparable with that of the cost of production at the Silesian Company's Works. The excess of expenditure, 2·75 francs, at the Lydognia Works, is made up of the following items:—Labour, 0·82 franc; repairs, 0·19; and general expenses, 1·74.

THE BELGIAN PROCESS OF EXTRACTING ZINC.

This process was first practised in the vicinity of Liège in the early part of the present century, but in what year I am unable to state. The ore formerly treated was exclusively calamine, of which large deposits once existed in the vicinity. The construction of the furnace and the distillatory apparatus have remained substantially the same to the present day, though both have been variously modified at different works. I have examined and compared many of the descriptions of this process; and I have had placed at my disposal sketches of one of the most approved furnaces of the Vieille Montagne Company, with all necessary measurements.[9] Extensive zinc-works, containing both Belgian and Silesian furnaces, have within a short period been erected near Swansea by Mr. Hussey Vivian. In 1848 I saw English, Silesian, and Belgian zinc-furnaces in the works then carried on by the late Mr. Vivian; but only the first were in operation. The engravings in illustration of the process in this work have been executed from working drawings of one of the largest Belgian furnaces yet erected, and I have reason to believe they are correct. Reduction is effected in vessels or retorts of refractory clay, closed at one end and open at the other, which is termed the mouth. In the mouth is adjusted a clay-nozzle, or condenser, on the free end of which is fitted a vessel of sheet-iron.

Retorts and appendages.—The retorts are cylindrical, *e*, *e*, *e*, figs. 146, 148.

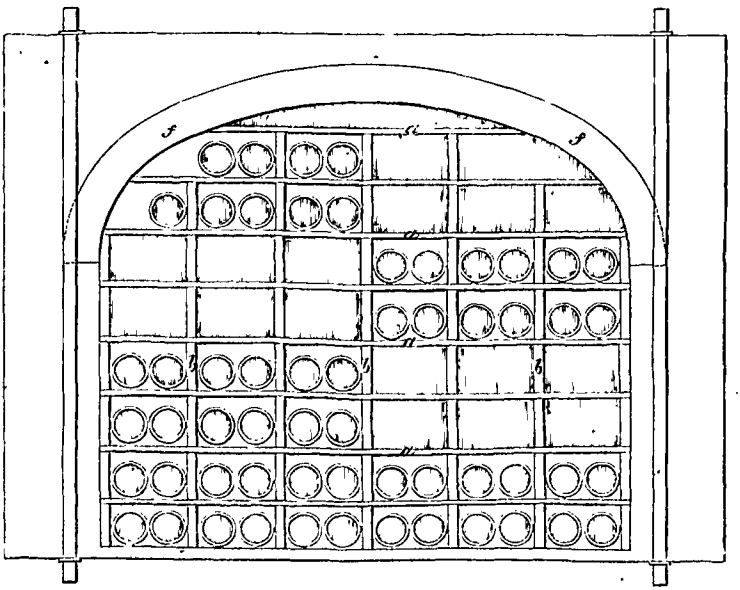

Fig. 146. Front Elevation. The furnace is shown as only partially filled with retorts; the shaded rectangular spaces indicate the empty compartments.

[9] By M. Eckart, to whom I have pleasure in acknowledging my obligation. Thum has recently published a description of the works of the Vieille Montagne Company, of which I have availed myself. Ueber den Zinkhüttenbetrieb der Altenberger Gesellschaft. Von Ingenieur W. Thum, Berg. u. hüttenm. Zeit. 1859-1860.

They are composed of the same materials, and fashioned in moulds constructed on the same principle, as those described under the Silesian process. The clay-nozzles, or condensers, have the form and dimensions shown in fig. 148, *i*, *i*, *i*, &c.: their transverse section is circular. On the outer ends of these nozzles are placed sheet-iron vessels, or

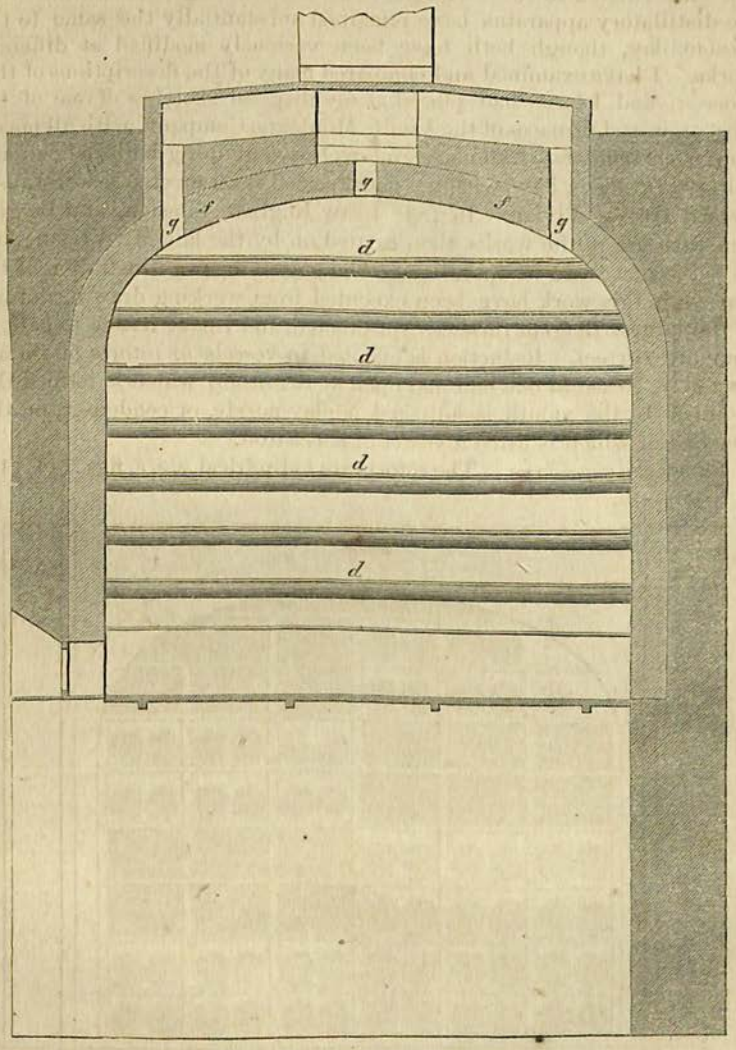

Fig. 147. Vertical Section on the line A B, fig. 150.

receivers, of which the form and dimensions are also shown in fig. 148, *l*, *l*, *l*: in the centre of the closed, or wide, ends of these receivers is a small hole, *m*. But it has, I believe, been found that this condensing apparatus may be replaced with advantage by the simple clay condenser in use at Stolberg, and which has already been described. In replacing

old retorts by new ones, the same precautions must be observed as in the Silesian process.

Description of the furnace.—The retorts are arranged in parallel rows one above another in a narrow vertical arched chamber, along the bottom of which is the fire-place. Fig. 146 is the front elevation; fig. 147 is a vertical section on the line A, B, fig. 150; fig. 148 is a vertical section on the line C, D, fig. 150; fig. 149 is the end elevation at the fire-place door; fig. 150 is a horizontal section immediately above the fire-bars on the line E, F, fig. 148. In front is a series of cast-iron plates, or shelves, inclining slightly forwards and downwards, *a*, *a*, *a*, &c., figs. 146, 148. On these plates, at regular distances, fire-brick slabs are placed on edge vertically and at right angles to the long axis of the fire-place, *b*, *b*, *b*, figs. 146, 148. On the upper and posterior edges of these slabs, where they extend behind the iron plates, other slabs of fire-brick are placed nearly horizontally, *c*, *c*, *c*, &c., fig. 148; the anterior edges of these slabs rest on the posterior edges of the iron plates, in the manner shown in fig. 148. A series of rectangular compartments is thus formed, within each of which the mouths of two retorts are contained. In the back wall of the furnace is a series of ledges, upon which the closed ends of the retorts are supported, *d*, *d*, *d*, &c., figs. 147, 148. The retorts incline downwards towards the front, *e*, *e*, *e*, fig. 148. By this inclination any corrosive slag which may be produced during the working of the furnace will flow forwards from

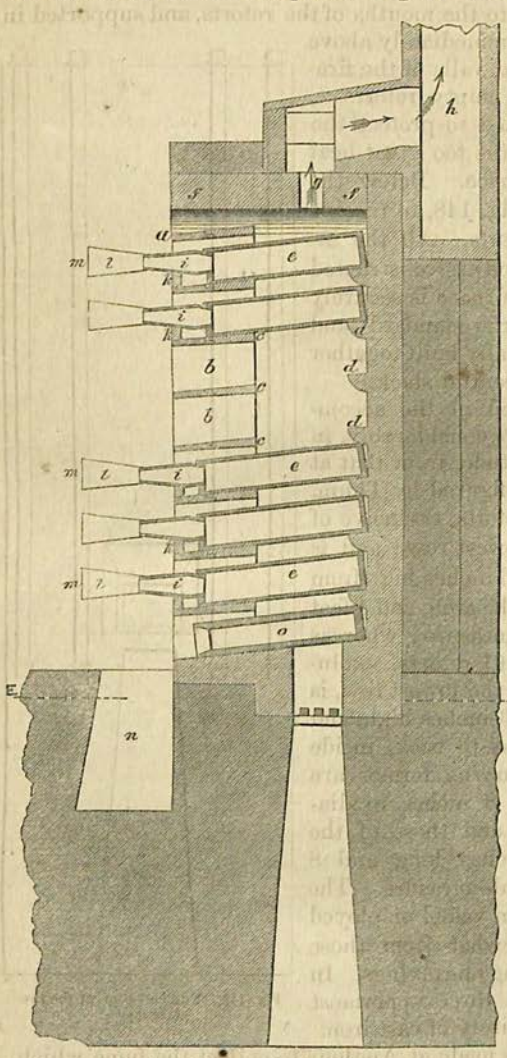

Fig. 148. Vertical Section on the line C, D, fig. 150.

the *hottest* towards the *coolest* part, where it would be less injurious. Clay luting is carefully applied round the mouths of the retorts, so as to prevent as completely as possible the passage of air through any part of the front of the furnace. In the arch *f*, *f*, figs. 146, 147, 148, are three flues, *g*, *g*, *g*, communicating with the stack, *h*. The clay condensers, *i*, *i*, *i*, fig. 148, are luted into the mouths of the retorts, and supported in front by bricks, *k*, *k*, *k*. Immediately above the fire, and resting on the walls of the fire-place, is a row of thick empty retorts, *o*, fig. 148, which are designed to protect the next row of retorts from the too great heat of this part of the furnace. Below the floor, in front, is a pit, *n*, fig. 148, to receive the residues from the retorts. All the internal parts of the furnace are constructed of good fire-brick. The furnace is securely clamped and braced by iron standards and tie-rods. Furnaces are usually built together in groups of four, with a central stack.[1]

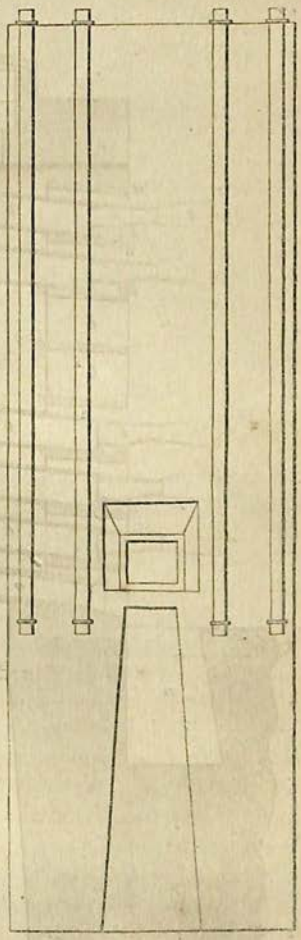

Fig. 149. End elevation at the fire-place door.

The furnace represented in the accompanying engravings differs considerably, in proportions and in magnitude, from that at Moresnet, described and figured by Thum. The former contains 78 retorts, exclusive of the empty ones in the lowest row; and is about 11 feet wide, 9 feet 6 inches high from the floor to the centre of the arch, and 4 feet from front to back, inside measure; whereas the latter contains only 61 retorts, exclusive of the empty ones in the lowest row, is about 8 feet wide, 10 feet 6 inches high, and 6 feet 6 inches from front to back, inside measure. The retorts in the former are 3 feet 6 inches long and 8 inches in diameter, outside measure; and those of the latter about 3 feet 3 inches long and 8 inches in diameter, outside measure. The clay-nozzle and sheet-iron vessel employed at Moresnet differ somewhat from those shown in the accompanying engravings. In the Moresnet furnace the three uppermost shelves (*a*, *a*, &c.) are entirely of cast-iron.

In 1857 an attempt was made at Angleur to collect the fume which, in spite of the sheet-iron vessels on the nozzles, escapes into the atmosphere. A hood of sheet-iron was suspended over the front of the furnace, and connected with the stack by a wide sheet-iron pipe. The result

[1] The apparatus used in charging is exactly similar to that previously described under the Silesian Process.

was not successful: no sensible amount of fume was recovered, and the men suffered much from the heat radiated upon their heads.

The following details concerning the working of the Belgian furnaces of the dimensions stated above, are extracted from Thum's description:—

The ore employed at Moresnet is calamine, which is calcined in circular kilns 2^m 20 (7 ft. 2 in.) in diameter at the mouth; 2^m 95 (9 ft. 8 in.) in diameter at the widest part, which is 2^m 14 (7 ft.) below the mouth; and 1^m 70 (5 ft. 6 in.) in diameter at the bottom, where four openings exist for drawing out the calcined ore. The bottom is conical, and the height of the cone is 1^m 05 (3 ft. 5 in.); and the height of the kiln, from the point of the cone to the mouth, is 5^m 35 (17 ft. 6 in.).

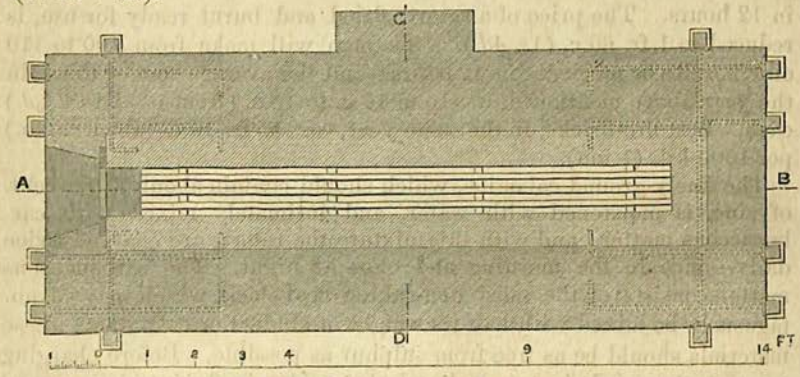

Fig. 150. Horizontal Section on the line E, F, fig. 148.

The ore is broken in pieces of about the average thickness of 0^m 15 (6 in.). The kiln is charged with alternate layers of inferior non-caking coal and ore. Calcined ore is drawn from 4 to 6 times in 24 hours, during which period 25,000 kil. (about 25 tons), on the average, are passed through the kiln, with a consumption of from 3 to 4 per cent. of coal.

The small ore which is obtained in the process of dressing is calcined in reverberatory furnaces. At Moresnet, large furnaces with double beds, one over the other, are employed for the purpose, as well as smaller furnaces heated by the waste gases of the reduction furnaces, and built on the top of the latter. The construction of the double-bedded furnaces is similar to that of the calciner described at p. 382. The beds are slightly elliptical on the sides, 5^m 90 (16 ft. 5 in.) long, and 2^m 20 (7 ft. 2 in.) broad in the widest part. The ore is first dried on the top of the furnace, and then allowed to fall upon the upper bed, where it is heated and carefully stirred during 6 hours, after which it is transferred to the lower bed, where it is again calcined during the same length of time. About 8000 kil. (8 tons) of calamine are calcined in one of these furnaces in the course of 24 hours.

Both the clay and the calamine are ground under edge-rolls of cast-iron revolving in pairs over beds of cast-iron plates. The rolls are 1^m 60 (5 ft. 3 in.) in diameter, and about 0^m 35 (about 14 in.) in breadth;

they weigh 3200 kil. (about 3 tons 2 cwt.) each. Under a pair of such rolls, from 15,000 to 18,000 kil. (about from 15 to 18 tons) of calcined calamine or clay may be ground in the course of 12 hours, and with a consumption of about 3-horse power.

At Moresnet the retorts are made by hand: one man will make from 18 to 20 in 12 hours. After having been dried and burnt ready for use, they cost on an average, in 1857, from 2 fr. (1*s.* 8*d.*) to 2 fr. 10 c. (1*s.* 9*d.*) each. At the Vieille Montagne Company's Works at Angleur and St. Leonard in Belgium, the retorts are made as follows:—A cylindrical mould, divided longitudinally into two equal parts, which may be clamped firmly together in the usual manner, is rammed full of clay and placed under a boring machine, when the interior is bored out. With two machines of this kind about 260 retorts may be made in 12 hours. The price of a retort, dried and burnt ready for use, is reduced to 1 fr. 60 c. (1*s.* 4*d.*). One man will make from 100 to 110 clay nozzles or receivers in 12 hours; and the average cost of these, in the year above mentioned, was from 14 c. to 16 c. (from $1\frac{4}{10}d.$ to $1\frac{6}{10}d.$) each. Best fire-bricks, in the same year, cost 55 fr. 19 c. (about 2*l.* 6*s.*) per 1000 kil. (1 ton).

The finely-ground calamine, which should contain about 50 per cent. of zinc, is moistened with water, and intimately mixed with carbonaceous matter; and with this mixture the retorts are charged twice daily—once in the morning and once at night. The carbonaceous matter consists of the most non-caking coal-slack, which may advantageously be mixed with half its weight of cinders or coke-dust: these materials should be as free from sulphur as possible. Before charging a retort, the nozzle is detached and the residue in the interior scraped out, the slaggy matter adherent to the inner surface of the retort being at the same time removed as completely as practicable. The matters thus drawn out fall into the pit *n*, fig. 148, from which they are subsequently conveyed away. The workmen, in charging the upper retorts, stand on a moveable platform with steps. After charging, the nozzle, smeared over with clay, is adjusted into the mouth of the retort, and a brick, *k*, fig. 148, is pushed under it. The sheet-iron receivers are placed on the nozzles when the vapour of zinc begins to appear. After the lapse of 6 hours most of the nozzles will be filled with melted zinc, which is withdrawn by means of a little scraper. This process is repeated before charging afresh.

Cracked or perforated retorts must be replaced by new ones, which have been previously gradually heated to redness in an adjoining kiln. This operation generally occurs every morning.

The lower rows of retorts, being exposed to a higher temperature than the upper ones, are more heavily charged than the latter. The retorts of the lower half of the furnace generally receive from 12 to $12\frac{1}{2}$ kil. ($26\frac{1}{2}$ to $27\frac{1}{2}$ lbs.), and those of the upper half from 6 to 7 kil. (13 to 15 lbs.), each. Less rich ores, and such as contain much basic matter like oxide of iron, which would attack the substance of the retorts at a high temperature, are generally introduced into the latter. Zinciferous matters, from which the metal may, on account of their rich-

ness, be separated at a gentle heat, are put into the upper retorts: they consist chiefly of the residues obtained in the treatment of zinc fume in the Montefiori furnace, and the crusts of oxide of zinc which are detached from the nozzles, and which in the course of time may accumulate to such an extent as to obstruct the passage and render them useless. Before using the nozzles it is customary to smear them over with milk of lime, with a view of causing these crusts a more easy separation.

At Moresnet, in a furnace such as has been described, 1200 kil. (about 1 ton 2 cwt.) of ore are treated in 24 hours; and the average yield of zinc, from ore containing 50 per cent., is from 450 to 470 kil. (from 922 to 963 lbs.), *inclusive* of that in the fume produced, and of which the greater part is obtained in the state of ingot by simple fusion in the Montefiori furnace. The actual yield of zinc from the ore is from 38 to 39 per cent.

In the following table by Thum are presented the average results of the working of one of the Moresnet furnaces during 24 hours, calculated from the actual results obtained during the first four months of 1857:—

Charge.		Produced.		Total yield of zinc °/₀	Fuel and materials consumed.			
Calamine.	Carbonaceous reducing matter.	Zinc.	Zinc fume.		Coal.	Retorts.	Nozzles.	Fire-bars.
kil.	kil.	kil.	kil.		kil.	Number.	Number.	kil.
1035	549	371	37	39·0	1479	3·8	11·5	0·3

Thus the amount of coal consumed (supposing the 549 of reducing agent to have consisted entirely of coal) for 1 ton of zinc is 5·46, or very nearly 5½ tons; and only 3·98 tons, exclusive of the coal used in reduction. But this does not include the coal consumed in calcination of the ore, and that used in the preparatory heating of the retorts; yet the amount seems very small.

In large zinc-works in this country, in 1859, the amount of coal consumed as *fuel*, in the extraction of 1 ton of zinc by the Belgian process, was stated to me to be 6¼ tons; but I think it must have exceeded this amount. I am informed (Nov. 1861) that the weekly production of zinc at one large establishment in this country is about 100 tons: both the Silesian and Belgian methods are employed; the cost of production by the former process is about 17*l.* per ton, and by the latter process about 18*l.*, inclusive of the cost of ore, &c.

From the preceding data it appears that with ore containing 50 per cent. of zinc, there is an average loss of zinc of from 11 to 12 per cent.; but of this at least half is recovered from the residua, the other half being irrecoverably lost, partly by volatilization from the nozzles, partly by the escape of zinc from bad retorts, and partly by imperfect reduction and the consequent loss of zinc in the residua from the retorts. Supposing that on an average not fewer than 3 retorts have daily to be replaced by new ones, and that each retort receives a

charge of 10 kil., then the constant loss of zinc by volatilization might be estimated, according to Thum, at 1·25 per cent.

Each furnace requires 4 men—2 head-men and 2 subordinates—of whom 2 are on duty at a time during a shift of 12 hours. The men receive a fixed sum in wages, and, in addition, an amount dependent on the zinc produced. At the end of every month, in addition to their fixed wages, they receive only half the amount which they may have earned in excess: the other half is not paid to them until 15 months afterwards, *i. e.* a quarter after it has become due. By this arrangement the men are stimulated by a regard for their own interest at all times to produce the greatest yield, to take care of their furnaces, and to retain their situations.

Carinthian method of extracting Zinc.[2]

This process was formerly practised in Carinthia and Hungary, but whether it has been entirely abandoned I know not. Reduction was effected in clay pipes or retorts set vertically in an arched chamber, heated by the flame of a wood fire, which I will call the reduction chamber. These pipes were 40 inches long, 4½ inches in diameter in the clear at the top and 3¼ at the bottom, and from ¼ to ⅜ inch in thickness. The narrow end of each pipe was fixed in a foot-piece of clay, consisting of a short vertical tube having at the top a square flange, also of clay. The flanges of these foot-pieces formed the bed of the reduction chamber; they were supported by a trellis of iron bars, and packed close together like the pieces of a mosaic pavement. The pipes being duly charged with the mixture of zinc-ore and carbonaceous matter, and closed at the top or wide end, the entrance into the reduction chamber was stopped and the fire lighted. The vapour of the zinc passed downwards, as in the English process, through the foot-piece, and condensed in drops on sheet-iron placed about 12 or 14 inches underneath to receive it. When the charge was worked off, the furnace was allowed to cool, in order that workmen might enter the chamber and prepare for the next charge. Thus the furnace did not work continuously, and there must, consequently, have been much waste of heat and loss of time. Both calamine and blende were employed. The calamine was calcined with wood in open kilns consisting of four walls, and was afterwards finely stamped or ground and sifted. The blende, after having been freed as completely as possible by hand from pyrites and vein-stuff, was roasted with wood and small charcoal in open walled kilns. The roasted mass was washed with water in order to dissolve out any white vitriol which it might contain; after which it was reduced to fine powder and roasted sweet in a reverberatory furnace: this required from 8 to 12 hours, with frequent stirring. The roasted blende was mixed with charcoal-dust and lime in fine powder, as obtained by slaking and reheating, and the whole was thoroughly kneaded with water containing in solution

[2] Tagebuch einer metallurgisch-technologischen Reise, durch Mähren, Böhmen, etc. Von Christian Fürchtegott Hollunder. Nürnberg, 1824, p. 373.

common salt and the soluble matter of wood-ashes. The actual quantities employed were as follow:—For ore sufficient to charge 336 pipes, 14 cubic feet of solution of wood-ashes, 26 lbs. of common salt, and 76 lbs. of lime. It was estimated that the solution contained about 4 lbs. of potash. The potash and the salt served the purpose of glazing the internal surface of the tubes and of thereby rendering them impervious to the vapour of zinc. Small pieces of charcoal of the size of hazel-nuts were mixed with the mass in order to loosen it and promote reduction. Each pipe contained from 5 to 6 lbs. of ore. The pipes, after having been properly burnt, were filled by means of a small shovel to within about 4 inches of the top or wide end with the mixture prepared as above described. Into the empty space thus left small pieces of charcoal were introduced, over which pieces of charcoal dipped in clay were placed crosswise so as completely to close the tube at this end. The charge was prevented from dropping down through the lower or narrow end by pieces of charcoal. A portion of the reduction chamber was set apart for burning unburnt pipes to be used in a subsequent operation. A single furnace at Dölach contained 84 pipes charged and 51 empty. At Dognacska in Hungary there were not fewer than 256 pipes in a single furnace.[3] The furnaces were built either in pairs or four together. After working off a charge the furnace was left to cool during 1 or 2 days, after which the whole of the pipes were taken out; the bad were replaced by freshly burnt ones, and the rest were used again. The furnace was lighted at 9 o'clock in the morning, and at 7 in the evening it began to yield zinc. At noon on the second day zinc was copiously produced; but the furnace was not considered as in proper working order until about 10 o'clock in the evening of this day. The whole time of distillation generally lasted from 30 to 40 hours. In extracting 1 centner of zinc at Dölach 180 cubic feet of wood were consumed.[4] The selling price of zinc (1824) was 3*l.* 6*s.* 8*d.* the centner (Bavarian), that is, between 60*l.* and 70*l.* per ton.

Zinc fume.—In the extraction of zinc from its ores a considerable quantity, as we have seen, of fume in the state of very mobile grey dust, is collected in the sheet-iron vessels attached to the nozzles or condensing-tubes in the Silesian and Belgian processes. It consists essentially of very finely-divided metallic zinc, intimately mixed with oxide; but it is also stated that certain foreign metals of frequent occurrence in zinc-ores—namely, cadmium, arsenic, lead, and (according to Thum) antimony—become concentrated in it.

Thum has published the following analysis, by himself, of the fume from the Silesian furnaces at Borbeck, in which calamine from Wiesloch is treated in admixture with many varieties of blende:[4]—

Zinc	97·82
Iron	0·16
Lead	0·23
Cadmium and arsenic	0·08
	98·29

The proportion of oxygen in combination with the metals is not given.

[3] Karsten, Sys. 4. p. 479.

[4] Berg. u. h. Zeit. 1859, p. 409.

In one place Thum states that the fume is pyprophoric, and, in another, that it takes fire in *moist* air and burns to oxide.[5] When fresh fume is heated to the melting-point of zinc, without access of air, and then subjected to pressure, the finely-divided particles of zinc unite into a liquid mass, leaving from 8 to 10 per cent. of oxide of zinc. Accordingly, a process (to be described presently) for the extraction of zinc from fume is founded on this principle.

The excessively minute particles of metallic zinc in the fume would appear to be kept from uniting during condensation by the interposition of a small quantity of oxide of zinc. It is easy to conceive how the latter may be generated by the action of the vapour of zinc on any carbonic acid which may escape along with it and the carbonic oxide from the retorts. The reduction of carbonic acid to carbonic oxide might thus be effected by the metallic zinc present, with the formation of an equivalent proportion of oxide of zinc, either by an alteration of temperature or a variation in the relative proportions of the carbonic acid, carbonic oxide, and vapour of zinc—changes of condition which may be supposed not only possible, but likely to occur. Thum attributes the formation of this oxide to the action of the vapour of water evolved from the coal used as the reducing agent; but the production of zinc fume takes place equally, I believe, when no water can be present in the retorts. Oxidation may be caused in a certain degree by the presence of atmospheric air in the condensing apparatus; yet, if I mistake not, and I am by no means sure on this point, fume will be formed even when atmospheric air has been perfectly excluded from this apparatus.

It has been recommended to employ the grey fume as paint, especially for the copper bottoms of ships; but it is generally utilized either by redistilling it in admixture with carbonaceous matter in the reduction furnace, or by adding it to the charge of ore prepared for reduction, or it may be subjected to special treatment in what is termed the Montefiori furnace. If the first plan be adopted, impure zinc is apt to be produced on account of the concentration of foreign metals in the fume; and the second plan is consequently preferred, as the influence of these foreign metals is rendered insensible by their diffusion through a large mass of zinc.

The Montefiori furnace.[6]—The vessel or pot in which the fume is heated is a hollow cylinder, closed at one end (the bottom) and open at the other (the mouth). The depth of the cavity is about 27 inches, and its diameter between 7 and 8 inches. On one side, at the bottom, is fixed on at right angles a tube, of which the bore widens upwards towards the junction of the vessel. Both the pot and the projecting tube are made of clay. Two parallel rows of these pots are set vertically on their closed ends in a rectangular chamber, having a partition-wall between them. Underneath the bottom of this chamber, which is flat, is a fireplace with an arched roof, extending in a direction parallel with the two rows of pots above. Flues pass through the roof of the fireplace into the chamber, which by this means is equably heated. The ends of

[5] Op. cit., p. 408, 409.

[6] Patented in this country by Jacob Levi Elkin, A.D. 1856. No. 2796.

the projecting tubes of the pots protrude through the outer or side walls of the chamber. The roof of the chamber is flat, and contains openings corresponding to the mouths of the pots, which remain open, and are thus easily accessible from the outside.

The pots are provided with cylindrical clay pieces, which fit into them like pistons; and to these pieces are firmly attached iron rods extending upwards considerably above the mouths of the pots: these rods pass through openings in bars of iron, fixed over the pots at a convenient height above the roof of the furnace; and on their upper or free ends suitable handles, with four arms placed crucially, may be fastened, so that the clay pistons may be easily pressed down and made to receive a circular motion.

The furnace being heated, and the ends of the projecting tubes having been stopped with clay, zinc fume is put into the pots, and the pistons of clay are pressed down upon it. After gently heating during 2 or 3 hours, and exerting pressure with the communication of an occasional rotatory motion to the pistons, the zinc is obtained in a liquid mass at the bottom of the pots, and may be withdrawn by unstopping the projecting tubes at the bottom. In each pot about 20 kil. of zinc fume may be thus treated at a time; so that in a furnace containing 12 of these pots, from 700 to 900 kil. of fume may be treated in the course of 12 hours.

The zinc separated directly by this process is stated to be quite as impure as that obtained by the distillation of the fume *per se*.

At Borbeck, where coal containing chloride of sodium is used, chloride of cadmium, in fine transparent crystals, has been observed to be deposited in very sensible quantities about the orifice of the projecting tubes in the Montefiori furnace.[7]

A specimen of fume which I collected on the arches near the condensing tubes of the English zinc furnace, which I saw in operation in 1859, has been imperfectly analysed in my laboratory by Mr. Weston. Its colour was dirty brownish grey. Blende was the ore employed. The following results were obtained:—

Oxide of zinc	46·70
Oxide of cadmium	16·23
Sesquioxide of iron	4·45
Alumina	0·75
Lime	1·43
Sulphur	0·82
Sulphuric acid	2·85
Organic matter (carbonaceous)	10·01
Hygroscopic water	1·98
Insoluble residue undetermined	7·94
	93·16
Unaccounted for	6·84
	100·00

FOREIGN MATTER IN COMMERCIAL ZINC, AND ITS INFLUENCE ON THE WORKING QUALITIES OF THE METAL.—Commercial zinc is never pure, and varies much in quality. Karsten has ascertained the effect of various metals on zinc,

[7] Thum, op. cit., p. 409.

and has also investigated the composition of different kinds of commercial zinc.[8] *Sulphur.*—Karsten never detected a trace of sulphur in any of the numerous specimens of zinc which he examined. According to Dr. Alfred Taylor, commercial zinc generally contains sulphur. A minute quantity of sulphur was detected in every specimen of the various kinds of commercial zinc examined by Eliot and Storer. *Arsenic.*—Karsten only sought for arsenic in varieties of zinc from Silesia, which could not be rolled without cracking; and he was not able to detect a trace. Schauffele states that he found arsenic in several kinds of commercial zinc, and determined the amount by Jacquelain's method, which consists in passing the hydrogen evolved by the action of dilute sulphuric acid upon the zinc through a solution of gold. His results are as follow:[9]—

		Arsenic in 1000 parts of zinc.
Silesian zinc	contained	0·0085
Vieille Montagne	,, ...	0·00522
Ditto Corfali mine	,, ...	0·00457
French	,, ...	0·019

Eliot and Storer appear to have investigated with great care the question of the presence of arsenic in zinc. They impugn the accuracy of the methods adopted by Schauffele, and consider his results unsatisfactory. The conclusion at which they have arrived after a long course of experiment with many different varieties of zinc is, "that much of the zinc of commerce is free from arsenic, or at least contains no arsenic that can be detected by the most delicate tests known for that metal." One specimen of Vieille Montagne zinc was found to be perfectly free from arsenic, but another specimen contained decided traces of it; it was detected in Silesian zinc; in zinc extracted from blende by the English process at the Mines-Royal Works, near Neath; in zinc extracted by the Silesian process from blende by Messrs. Dillwyn and Co., Swansea; in zinc stated to have been extracted from silicate of zinc, near Wrexham; in zinc produced by Messrs. Vivian, Swansea; one specimen of Pennsylvanian zinc was perfectly free from arsenic, while another contained it; the New Jersey zinc, extracted from red zinc ore, contained an unusually large proportion of arsenic. Of the four samples of English zinc examined, "that of the Messrs. Vivian contained the most arsenic; 200 grammes of this spelter yielded an enormous mirror of arsenic in less than 10 minutes, and in a few minutes more a second mirror, large enough to give the characteristic odour."[1] A portion of arsenic is retained in the insoluble matter left by the action of hydrochloric or dilute sulphuric acid on zinc. *Tin.*—Eliot and Storer obtained decided evidence of the presence of tin in the zinc of New Jersey and in that of Messrs. Vivian, while in others they either failed to detect it, or only found "faint traces" of it. Karsten found that when the best Silesian zinc was alloyed with only 1 per cent. of tin, it was brittle at the

[8] Ueber die Beimischungen welche die Festigkeit des Zinkes vermindern. Archiv. 1842, 16. p. 597-632.

[9] Liebig u. Kopp, Jahresb. for 1850. p. 320.

[1] Op. cit., p. 87.

temperature at which zinc is malleable; and that it could only be rolled into sheet at a much lower temperature, and then not without splitting considerably at the edges. *Bismuth and antimony.*—Neither was detected by Karsten in Silesian zinc. *Copper.*—Not a trace was found by Karsten in Silesian zinc. Eliot and Storer found not the slightest evidence of the presence of copper in any zinc except that of New Jersey. According to Karsten zinc containing ½ per cent. of copper is harder and more brittle than ordinary zinc; it can only be rolled with difficulty, when it breaks easily and splits much at the edges, and the sheet zinc produced cannot be corrugated without breaking. *Silver.*—None was detected by Karsten in Silesian zinc. *Iron.*—Zinc and iron alloy easily, and commercial zinc is rarely free from iron. Karsten never found more than 0·24 per cent. of iron in any zinc; but a specimen of Silesian zinc which I procured at M. Lemanski's zinc rolling-mills in London contained not less than 1·64 per cent.: it was pronounced unfit for rolling. Eliot and Storer found 0·21 per cent. of iron in New Jersey zinc, and from 0·05 to 0·07 per cent. in sheet zinc procured in Berlin. The presence of iron is indicated by minute grey specks on the bright cleavage-planes of the freshly fractured surface of an ingot of zinc. Iron increases the hardness of zinc, and causes it to heat so much in rolling that in order to prevent cracking, it is necessary to allow the metal to cool sufficiently from time to time during the process. In the unannealed state the rolled sheet is extremely rigid and strong. According to Karsten, iron is very injurious in zinc intended for rolling when much lead is present; and zinc containing much iron and not more lead than exists in the best kinds of zinc, which are almost free from iron, is quite unfit for rolling. The proportion of iron in zinc intended for rolling, Karsten further states, should never exceed 0·2 per cent.; and it should never be accompanied with a greater amount of lead than is usually found in the best qualities of zinc. Zinc may be perfectly freed from iron by re-distillation in clay retorts, care being taken to prevent contact of the distilled metal with iron. *Cadmium.*—Zinc in the state in which it is condensed in the process of reduction, or, as it is termed, *rough* zinc, always contains cadmium, which, being by far the most volatile and most easily oxidisable of the two metals, may be separated in a greater or less degree from zinc by simply keeping it melted during a sufficient time in a reverberatory furnace. In 1829 Mentzel published an account of experiments which he had made at the Lydognia Zinc-works in Upper Silesia to ascertain the effect of cadmium on the malleability of zinc.[2] He found that, although cadmium increases the hardness and brittleness of zinc, an alloy consisting of 85 per cent. of zinc and 15 of cadmium could yet be rolled to the thickness of a line (about $\frac{1}{12}$ inch) without cracking; and he states what seems rather anomalous, namely, that this alloy is not more brittle than zinc containing 10 or only 5 per cent. of cadmium. There is no reason for believing that cadmium, in the small proportion in which it occurs in commercial zinc, exerts

[2] Karsten's Archiv. 1829, 1. p. 416.

any sensible effect upon the malleability of the metal. *Lead.*—This metal is generally, if not always, present in commercial zinc, and, according to Karsten, in proportions varying from 0·3 to 2·0 per cent. The following table contains Eliot and Storer's quantitative determinations of lead in various kinds of zinc :—

	Lead per cent.		Lead per cent.
Silesian	1·46	From Paris[6]	0·106
Vieille Montagne	0·292	From Berlin, in sheet	1·297
New Jersey, from red oxide	0·079	Wrexham, from silicate of zinc	1·192
Pennsylvania, from silicate of zinc	0·00	Mines Royal, from blende	0·823
Vieille Montagne, used at the U. S. mint	0·494	Dillwyn and Co., from blende	1·661
		Messrs. Vivian	1·516

[6] Sold as *pure* by Rousseau frères.

The dark grey residue obtained by the action of dilute sulphuric acid on commercial zinc consists chiefly of lead. When zinc and lead are melted together, they separate more or less completely during solidification; and when zinc containing lead is kept long melted without being agitated, the lead tends to subside. But zinc cannot be perfectly deprived of lead in this manner.

I am indebted to Messrs. Matthiessen and Bose for the following results. Lead and zinc were melted together in various proportions in a Hessian crucible over a large air-gas burner, stirred during a quarter of an hour with a tobacco pipe stem, and then allowed to remain at rest in a fused state during half an hour, a jet of coal-gas being all the while directed on the surface of the melted metals. The metallic mixture was poured into a porous cell previously heated to redness in a large crucible filled with sand. The weight of each casting was about 300 grammes (about 10½ ozs. avoird.), the height 100^{mm} (4 inches), and the diameter 25^{mm} (1 inch). After cooling and breaking the cell, the upper part of the metal was broken by the blow of a hammer from the lower one. Solidification of the metals generally occurred in about 2 hours after casting. Experiments were made to ascertain whether a more perfect separation would take place by keeping the metallic mixture liquid during a longer time; but this was not found to be the case.

In each case a portion was taken for analysis from the middle of the upper or *zinc end*, avoiding the outside; and another portion from the lower or *lead end*.

TABLE OF RESULTS WITH LEAD AND ZINC.

Lead 50 per cent.	Lead end	Zinc per cent.	1·62
Zinc 50 do.	Zinc end	Lead do.	1·22
Lead 66·6 do.	Lead end	Zinc do.	1·62
Zinc 33·3 do.	Zinc end	Lead do.	1·20
Lead 4 do.	Top	Lead do.	1·20
Zinc 96 do.	Bottom	Do. do.	1·17
Lead 96 do.	Top	Zinc do.	1·63
Zinc 4 do.	Bottom	Do. do.	1·79

Similar experiments were made with zinc and bismuth, and the results will be found in the following table:—

TABLE OF RESULTS WITH ZINC AND BISMUTH.

Bismuth 50 per cent. ...	Zinc end	Bismuth per cent.	2·42
Zinc 50 do. ...	Do.	Do.	do.	2·48
	Bismuth end	Zinc	do.	13·85
Bismuth 50 do. ...	Zinc end	Bismuth	do.	2·39
Zinc 50 do. ...	Bismuth end	Zinc	do.	8·65
Bismuth 80 do. ...	Top	Zinc	do.	14·0
Zinc 20 do. ...	Do.	Do.	do.	14·1
	Bottom	Do.	do.	12·93
	Do.	Do.	do.	13·1
Bismuth 80 do. ...	Top	Do.	do.	16·3
Zinc 20 do. ...	Bottom	Do.	do.	13·3
Bismuth 80 do. ...	Top	Do.	do.	14·1
Zinc 20 do. ...	Bottom	Do.	do.	8·8
Bismuth 5 do. ...	Top	Bismuth	do.	2·38
Zinc 95 do. ...	Bottom	Do.	do.	2·40

The conclusions which Messrs. Matthiessen and Bose draw from the preceding results are—

1. That at a temperature of a large air-gas burner lead will only dissolve 1·6 per cent. of zinc, and zinc only 1·2 per cent. of lead.

2. That bismuth under the same conditions will dissolve from 9 to 14 per cent. of zinc, and zinc 2·4 per cent. of bismuth.

Karsten inferred that lead may be present in zinc in two distinct states — one in which it is wholly combined with the zinc, and the other in which an alloy of lead and zinc is mechanically diffused through the mass of the zinc. The first condition is stated to occur when fusion takes place at a high temperature and is followed by extremely rapid solidification: the metal thus obtained is hard, and dissolves easily in dilute sulphuric acid with the formation of a pulverulent residue of lead. The second condition is stated to occur when fusion likewise takes place at a high temperature, but is followed by very gradual solidification: the metal in this case is soft, and dissolves slowly in dilute sulphuric acid with the formation of a flocculent or riband-like residue of lead in combination with a little zinc, which only becomes converted into powder by the prolonged action of the acid. With respect to the influence of lead upon the malleability of zinc and the quality of sheet-zinc there has been great difference of opinion. Zinc containing as much as 3 per cent. of lead has been rolled into sheet without cracking; and it has been stated that zinc strongly impregnated with lead may be more easily and better rolled into sheet than purer and harder zinc, but that the tenacity of sheet-zinc decreases in proportion to the amount of lead which it contains.

Karsten asserts that the presence of about 1½ per cent. of lead renders sheet-zinc tender and unsuitable for most kinds of work; and suggested that the peculiar states of combination in which he supposed lead to

be capable of existing in zinc, might exert a decided effect on its malleability; but we have seen that the malleability of the metal is remarkably affected by the mere conditions of temperature under which it is melted and allowed to solidify, so that possibly Karsten in his experiments may have ascribed to the presence of lead what was due exclusively to varying conditions of temperature.

In preparing ingots of zinc for rolling, care is taken to allow the lead to subside as completely as possible from the melted zinc. Preparatory to casting into ingots, the zinc is kept melted in large quantity in a reverberatory furnace, of which the bed inclines from the fire-bridge, so as to form a tolerably deep cavity or well at the opposite end, where there is an opening through which the metal is laded out. A considerable quantity of lead subsides and accumulates at the bottom of this well, and is from time to time removed. The temperature of the melted metal, it is hardly necessary to observe, is considerably below that at which ignition would occur. The ingots of zinc are thrown on the upper part of the bed near the fire-bridge, and are allowed to melt down gradually. If in lading any lead should accidentally be poured into the ingot mould along with the zinc, it will appear in ribands or strips upon the surface of the rolled sheets.

The various Methods of extracting Zinc compared with each other.

I should require more precise and far more numerous data than I possess at present in order to enable me to discuss this subject in a satisfactory manner. Much has been written upon it, different conclusions have been arrived at, and different reasons have been assigned for the selection of one process in preference to another. Yet there are points on which all persons who have had experience in the extraction of zinc seem to be pretty nearly unanimous. It may be advisable to examine the question under the following heads:—Consumption of Fuel, Consumption of Refractory Clay, &c., Cost of Labour, and Nature of the Ore. I shall exclude from consideration the Carinthian process, because the disadvantage resulting from its intermitting character, and the consequent alternate cooling and reheating of the furnace, is so manifest as to place it out of comparison with the other three processes described.

Consumption of fuel.—It is decidedly much greater in the English process than in either the Silesian or the Belgian. We have seen that in the treatment of the poor ores in Silesia, yielding less than 20 per cent. of zinc, not so much coal is consumed as in the treatment of ores in the English furnace, yielding more than 40 per cent. of zinc. With ores of the same character and richness, the consumption of fuel is very sensibly less in the Belgian than in the Silesian furnace.

Consumption of fire-clay, &c.—It is greater in the Belgian than in the Silesian process, *cæteris paribus*. I have not exact information as to the amount of consumption under this head in the English furnace.

Cost of labour.—The *amount* of labour required is, I believe, greatest in the Belgian process and least in the English. Moreover, in the former, the work is harder, and the men suffer more from heat, than

in either of the other two processes: indeed it is stated that in hot weather it is sometimes difficult to retain men at work at the Belgian furnaces. This circumstance might be expected to increase the cost of labour in the Belgian process, as compared with the other two. On the other hand, in a *given time* the largest yield is obtained from the Belgian furnaces. But this advantage is in a greater or less degree counterbalanced by the fact that the Silesian furnaces may be kept uninterruptedly at work during a longer period than the Belgian, which require more frequent reparation than the former. In the management of the Belgian furnaces more skill is said to be required than in the case of the Silesian.

Nature of the ore.—When an ore contains much foreign matter, such as oxide of iron, which exerts a corrosive action on the retorts, the Belgian process is recommended, because the contact of this matter would be least prolonged in this process, in which the retorts are most frequently cleaned out; and because, owing to the comparatively steep inclination of the retorts, any corrosive slag which may be formed would flow more readily towards the lower and cooler parts, where it would produce less mischief. The varieties of calcined blende employed are apt to be contaminated with oxide of lead, as well as oxide of iron; and on this account the Belgian process has been preferred for this class of ores. It is requisite, in the case of blende, that the ore should be calcined as sweet as possible; and in order to this, it must be reduced to fine powder. The internal surface of the retorts will therefore be exposed to greater contact in the case of blende than in the case of calamine, which is only reduced to the size of hazel-nuts; but the greater the contact, the greater will be the amount of corrosion of the substance of the retorts—an evil which will be less in Belgian than Silesian retorts, for the reasons above assigned.

My friend Dr. Astley Price, Ph. D., informs me that the corrosive action of any zinc-ore upon the substance of the retorts may be entirely prevented by heating the ore, mixed with coal-tar, in close vessels, so as to carbonize the tar. He had procured a patent for the process in 1858;[3] but previously, in 1856, Messrs. George and John Darlington had claimed the use of tar in admixture with zinc-ores in a provisional specification.[4]

In the selection of a locality for the erection of zinc-works, it is essentially requisite not only that the ore should be delivered at a reasonable price, but also that *good coal* and *very superior fire-clay* should be obtainable at a reasonable price.

According to the experience of the Vieille Montagne Company, zinc can only be profitably extracted when the price of coal does not exceed 15 fr. per 1000 kil. (12*s.* 6*d.* per ton), and that of fire-clay 35 fr. per 1000 kil. (1*l.* 9*s.* 2*d.*); and the ores, at the above-mentioned prices of coal and fire-clay, should on an average not contain less than 45 per cent. of zinc.[5] It has been ascertained at the works of this Company,

[3] A.D. 1858. No. 828. [4] A.D. 1856. No. 1619.
[5] Thum, op. cit., 1860, p. 101.

where both the Silesian and Belgian processes are conducted, that greater consumption of coal in the former is, with respect to value, equivalent to greater consumption of clay in the latter,[6] and that the cost of production is about the same in both processes. If we know, therefore, the relative consumption and actual prices of clay and coal in these processes, it is easy to select that which, *cæteris paribus*, will yield the most profit.

Alleged Improvements in the Extraction of Zinc.

Several patents have been obtained for effecting the reduction of zinc from its ores in blast-furnaces, and collecting the volatilized metal in various kinds of condensing apparatus; but I am not aware whether any of the methods specified have been tried on the large scale. It is, however, certain that not one of them has come into use. Although the ores might be readily reduced in a blast-furnace, yet there would assuredly be great practical difficulties in condensing the metal without considerable loss. The vapour of the zinc would issue from the furnace in admixture with a large volume of uncondensable gases; and this condition would render the condensation and *economical* collection of the metal extremely difficult, if not impossible, on the large scale. Of this we shall hereafter have ample proof when we examine the subject of the collection of the fume produced in lead-smelting. Costly contrivances have been adopted in order to catch this fume, and yet scarcely one has proved efficient in preventing the escape of an enormous quantity of lead into the atmosphere. We shall also find that precisely the same difficulty is experienced in collecting mercury when it is volatilized in admixture with the gaseous products of the combustion of fuel. While I do not venture to predict that the blast-furnace will never be successfully applied in the extraction of zinc from its ores, yet I confess I do not see much reason to anticipate improvement in that direction. The large experience which we now possess concerning the metallurgy of zinc would rather encourage us to hope for further improvements in the construction of the reduction-furnaces and in the mode of applying heat. As I have stood by the hot-blast stoves of some of the great South Welsh iron-works, which are heated exclusively by the combustion of the waste-gases of the blast-furnaces, it has often struck me that this mode of heating would be peculiarly well adapted to zinc reduction-furnaces. The temperature is remarkably uniform through the interior of these stoves, and there would appear to be no difficulty in raising it to a degree amply sufficient to reduce oxide of zinc; for I am assured that by suitably regulating the supply of gas and atmospheric air, the fire-brick lining of the stoves may even be melted. It would be possible, I think, with the use of this gaseous fuel, to construct a zinc reduction-furnace of large dimensions, either on the Silesian or Belgian principle, which should combine the most favourable conditions for the extraction of zinc from its ores, namely, a suffi-

[6] Thum, op. cit., p. 101.

ciently high and perfectly equable temperature with the capability of regulating it to a nicety.

Some years ago a gas-zinc-furnace was constructed by Mentzel on the Silesian principle, at the Lydognia Works,[7] and was reported by him to be successful; but as I have found no mention of such a furnace in any recent description of these works, I presume that on further trial the result proved unfavourable. The furnace resembled an ordinary Silesian furnace, with the exception that the fireplace was replaced by a deep chamber or gas-generator, for the production of the gas (see p. 200, *ante*); and there were several air-flues in the walls of this chamber, which proceeded from below upwards and supplied air, necessary for the combustion of the gases, in the immediate vicinity of the retorts. I may be wrong in inferring that the experiment at the Lydognia Works was a failure. However this may be, I still have a strong impression that gas-zinc-furnaces will one day be adopted. It may require a considerable outlay in making the requisite experiments on the construction of such furnaces, and success may only be attained after numerous failures.

The silicate of zinc, or electric calamine, of which I believe considerable quantities are still thrown away in this country, and which is frequently a constituent of common calamine, is, I am informed by Professor Brush, employed with success as an ore of zinc in the United States; and some years ago I received from Mr. J. A. Phillips a specimen of zinc extracted, on the large scale, in North Wales from the same description of ore. This zinc, however, was not so free from iron as we were led to anticipate; but this no doubt depended on the apparatus used to effect condensation, or on that used in the process of remelting, and was in no degree caused by the nature of the ore. We have seen that the oxide of zinc in electric calamine may be *completely* reduced by charcoal alone at a high temperature; but in the retorts of ordinary zinc-furnaces, it is stated that any silicate of zinc which may be present in the ores remains unreduced. To effect reduction by carbon alone, the temperature must not only be very high, but the mixture must be very intimate. Probably the best method of operating on electric calamine would be to mix it thus intimately with the carbonaceous reducing agent and lime, or lime and clay to furnish base for the saturation of the silica.

METHODS OF ASSAYING ORES OF ZINC.

The ores with which the assayer has to do are—

Calamine, raw or calcined.
Blende, raw or calcined.
Red oxide of zinc.
Silicate of zinc.

Formerly the assays were made by the "dry way," *i. e.* by exposing the ore in admixture with charcoal or other reducing agent to a high

[7] Karsten, Archiv. 2. B. 23.

temperature, and determining the amount of zinc by loss; and when the ores are rich in zinc and free from volatile metallic impurities, the per-centage obtained will approximate to the correct amount. The process is still occasionally resorted to by some assayers, and may be conveniently applied when liquid reagents are not at hand. It may be conducted thus:—50 grs. of ore are calcined "sweet," and the calcined product is weighed and mixed with from 10 to 15 grs. of charcoal-powder (of which the amount of ash which it leaves on burning has been previously ascertained), and the mixture is exposed, in a closed brasqued[8] clay crucible, to a high temperature for about half an hour. The residue from the cavity of the brasque is recalcined and weighed; and from the weight is deducted the amount of ash derived from the charcoal; and the difference between the weights found after the first and second calcinations will be equivalent to the amount of oxide of zinc reduced and volatilized. This oxide is composed of 1 part of oxygen by weight, and 4 parts of zinc; so that the weight lost by volatilization, minus $\frac{1}{5}$, will give the amount of zinc contained in the weight of the ore employed in the process. The actual results yielded by an assay on this principle are presented in the following tabulated form:—

	Grains.	
50 grains of calamine after calcination weighed.....	33·50	
The calcined residue, after exposure of the roasted ore to a high temperature in admixture with charcoal (minus the weight of ash in the quantity of charcoal used), weighed.....	10·30	
Oxide of zinc reduced and volatilized, *i.e.* Loss.....	23·20	
Deduct $\frac{1}{5}$ for oxygen.....	4·64	
50 grains of ore contain of zinc.....	18·56,	or 37·12 %

A covered clay crucible may be substituted for one lined with carbon; but in that case a larger amount of charcoal or other carbonaceous reducing agent must be mixed with the calcined ore. When much oxide of iron is present, it will be reduced with the formation, if the temperature be high, of minute globular particles of iron, and the result will accordingly be vitiated.[9] When lead is present as galena, it is converted, during calcination, into oxide and sulphate of lead, which, on subsequent heating with carbon, become reduced to metallic lead and sulphide of lead respectively, and, in the presence of iron, to metallic lead and sulphide of iron. When present as carbonate of lead, the latter is changed by calcination into oxide, which is subsequently reduced by the carbon with the separation of lead. A considerable amount of lead is also volatilized during the fusion; and the loss from this cause, together with the reductions just mentioned, renders the

[8] The brasque should be solid, and may be conveniently made of charcoal powder moistened with treacle. (See Crucibles, &c., *ante*.)

[9] A correction may be made by extracting the globules of iron with a magnet, and deducting an equivalent amount of sesquioxide of iron.

assay worthless. If the ore is a silicate, or contains silicate of zinc, the oxide of zinc, in combination with the silica, will be completely reduced by the charcoal, if the conditions are correct, and a skeleton of silica be left; and if lime is present, a residue of silicate of lime will be obtained.

The proportion of zinc in blende may, in the absence of volatile impurities, be determined by exposing a known weight of the pulverized blende, in admixture with a small quantity of charcoal, to a high temperature in a closed brasqued crucible. If the blende is pure, it will be completely reduced and volatilized; but when iron is present, a fused button of sulphide of iron will remain. The loss in weight indicates the amount of the sulphide of zinc, which contains 67 % of zinc.

By Sulphide of Sodium.

This is the most direct, quickest, and most practical method for the estimation of zinc in ores of zinc; and it is accordingly that which is now generally employed for commercial purposes. It is capable of yielding results within a few tenths per cent. of the amount of zinc obtainable by analysis. When a solution of sulphide of sodium is added to an ammoniacal solution of zinc containing a small amount of hydrated oxide of iron, the zinc is precipitated as white sulphide of zinc, and afterwards the suspended oxide of iron becomes blackened by the slight excess of sulphide of sodium which may have been used. By ascertaining how much of a standard solution of sulphide of sodium is required exactly to precipitate the zinc from the ammoniacal solution of a known weight of the metal, it follows that by a comparative experiment on a given weight of ore, the amount of zinc present in an ore may be determined.

For this method, solutions of sesquichloride of iron and sulphide of sodium are required.

The *dilute solution of sesquichloride of iron* may be prepared as follows:—50 grs. of hæmatite in powder (Fe^2O^3) are to be dissolved in hydrochloric acid; or 35 grs. of iron-wire may be dissolved in nitro-hydrochloric acid, and the solution afterwards diluted with water to 1 pint: 50 grs. of this solution will contain about 0·2 of metallic iron.

Standard Solution.—1400 grs. of crystallized monosulphide of sodium (NaS, 9 HO) are dissolved in 4 pints (35,000 grs.) of water. This salt is very soluble in water, and the solution, which should be clear and colourless, is ready for immediate use. The solution should either be filtered, or the clear supernatant liquor decanted off from any small amount of black precipitate which may be occasionally present. It should be kept in bottles of glass free from lead. An objection against the use of this solution is its liability to slow decomposition, so that it requires to be re-standardized every third or fourth day. A quantity of solution prepared and employed for assaying had the following standard: 1000 grs. = 10·03 grs. of zinc; after the lapse of 15 days 1000 grs. = 9·31 grains of zinc. In practice, where many assays have to be made, this liability to decomposition is immaterial, as the solu-

tion can readily be re-standardized; or not more solution need be prepared at a time than is sufficient for a given number of assays. When crystallized sulphide of sodium cannot be obtained, about 2000 grs. of caustic soda are to be dissolved in 1 pint of water, and the solution is to be divided into two equal portions. Through one of these portions sulphuretted hydrogen gas is passed until saturation occurs; it is then added to the other portion, when the strength of the sulphide of sodium solution thus prepared must be approximately found, after which it must be diluted with water until it is reduced to the proper strength. The solution may be standardized, as follows: 2 or 3 pieces of pure zinc, varying from 5 to 10 grs. each in weight, are dissolved in separate portions of dilute hydrochloric acid, containing a few drops of nitric acid; each solution is put into a separate flask and diluted with water until it occupies about three-quarters of a pint in volume; 50 grs. of the dilute solution of sesquichloride of iron, and afterwards ammonia in excess, are added to each solution in succession. The solution of sulphide of sodium from a graduated burette is slowly allowed to run into the cold ammoniacal solutions until the zinc is completely precipitated, and the flocculent sesquioxide of iron blackened. The number of divisions of the solution in each flask used is then read off, and the mean of the numbers is taken as the standard. For example—

Zinc.		Number of Divisions.		200 Divisions (1000 grs.) of solution of sulphide of sodium are equal to	
5·885 grs.	required	117	therefore	10·06	grs. of zinc.
7·960	„	159	„	10·01	„
	Mean number or standard			10·03	

Process.—From 10 to 50 grs. of the ore are to be heated with hydrochloric or sulphuric acid and a small quantity of nitric acid, a large excess of acid being avoided; when decomposition is complete, the solution is diluted with a small quantity of water; ammonia and carbonate of ammonia in excess are poured in, and the whole is digested at a gentle heat during 20 or 30 minutes, and afterwards filtered into a pint flask, and the residue on the filter washed with warm ammoniacal water. To the ammoniacal filtrate, which should measure about three-quarters of a pint, are added 50 grs. by measure of the solution of sesquichloride of iron to which ammonia has been previously added. When the solution is *cold*, the measured solution of sulphide of sodium from the burette is slowly and cautiously dropped in, while the ammoniacal solution is kept in *constant motion*, until the white precipitate of sulphide of zinc assumes a greyish black colour from the blackening of the flakes of sesquioxide of iron in suspension. The number of divisions of the solution of sulphide of sodium used is then read off, and from the standard the percentage of zinc is calculated. For example: 200 divisions (1000 grs.) of standard solution = 10·03 grs. of zinc, and 20 grs. of ore required 170 divisions of the same solution.

200 : 170 : : 10·03 : 8·53
8·53 × 5 = 42·65 % of zinc.

It is desirable to have the oxide of iron present in a flocculent condition: it is therefore better to add ammonia to the measured quantity of sesquichloride of iron, before mixing it with the ammoniacal solution of zinc; for if the sesquichloride is added direct, the oxide of iron coagulates. Instead of the sesquichloride, tartrate of ammonia and iron or tartrate of potass and iron may be added, when the iron will remain in solution; good results may be thus obtained, but not better than with the flocculent oxide of iron. Although it is possible to make correct assays, after a little practice, with variable amounts of oxide of iron present in the ammoniacal solution, by stopping the assay at the proper tint, which will vary according to the amount of iron present, yet the use of the flocculent oxide is preferable.

It is necessary to agitate the ammoniacal solution continually during the addition of the sulphide of sodium; otherwise the oxide of iron is liable to be blackened before the complete precipitation of the zinc as sulphide, by coming in contact with the sulphide of sodium as it enters the solution. If the oxide of iron becomes thus blackened, the assay is spoiled; but this difficulty will not be experienced if the assay is properly managed. The change of tint of the oxide of iron from reddish-brown to black is best observed by transmitted light; and when darkening begins to appear, the sulphide of sodium should be added drop by drop until the proper point, when the blackening will occur rapidly.

There is a slight error owing to the retention of a small quantity of zinc in the residue after digestion in ammonia and carbonate of ammonia; but it is practically unimportant, and is compensated for by the slight excess of sulphide of sodium used in blackening the oxide of iron at the completion of the assay.

Precautions to be taken in the presence of the following metals:—

Iron.—This metal is often present in ores of zinc, in calamine as sesquioxide and carbonate of protoxide, and in blende as sulphide. When it occurs in small quantity the assays may be made without any filtration; but it is better always to filter off and add a definite amount of iron to each assay. If the iron present is considerable, on addition of the ammonia, it is apt to retain some oxide of zinc; and in this case after decanting off the ammoniacal solution it is better to treat it a second time with ammonia and carbonate of ammonia previously to filtration.

Manganese.—It is present in red oxide of zinc, calamine, &c. On the addition of carbonate of ammonia, the manganese will only be partially separated; but the addition of a few drops of bromine to the ammoniacal solution will ensure its complete precipitation.

Copper.—It is occasionally present as carbonate in calamine, or as copper pyrites in blende. It communicates a violet or blue colour to the ammoniacal solution. When present in small quantity, it may be separated conveniently by adding a few drops of the sulphide of sodium to the *hot* filtered ammoniacal solution of zinc, until the colour is discharged, and afterwards filtering rapidly. The zinc can now be estimated in the filtrate when cold. If copper is present in con-

siderable quantity, the ore must be treated with dilute sulphuric acid, and the copper precipitated from the solution of sulphate of zinc thus obtained by means of a piece of clean bright iron. The precipitated copper may be washed, dried, and weighed, if necessary. The solution freed from copper is heated with a small quantity of nitric acid in order to peroxidize the iron, after which the assay may be proceeded with in the manner described.

Lead.—It is sometimes present as carbonate of lead in calamine, or as galena in blende. A portion of the metal will be left in the insoluble residue as sulphate, and the remainder will be precipitated on the addition of the ammonia and carbonate of ammonia, so that lead does not interfere with the assay.

Silver.—It is occasionally present in blende. In the presence of dilute hydrochloric acid, it will be left in the insoluble residue, which should be separated by filtration *before* the addition of the ammonia, &c.; but it is seldom present in sufficient quantity to interfere with the assay.

Cadmium.—It is occasionally present in small quantity; it is not soluble in the ammoniacal solution containing carbonate of ammonia, and, therefore, does not interfere with the assay.

Method of assay by dissolving out the oxide of zinc by means of solution of ammonia and carbonate of ammonia.—This method only yields approximate results, but it is nevertheless useful when sulphide of sodium is not at hand. It answers pretty well for tolerably pure ores; but when other matters are present, especially oxide of iron, the error is increased in proportion to the amount of iron present. The process is conducted as follows:—From 20 to 50 grs. of the finely powdered ore are weighed out in a porcelain capsule, and calcined completely in a muffle or over an air-gas burner, and the weight of the calcined ore is taken. This is digested in a beaker or flask at a gentle heat, with a solution of ammonia and carbonate of ammonia, for about 20 minutes. The insoluble residue is collected on a filter, washed with hot ammoniacal water, dried, ignited, and weighed. The weight of the residue thus obtained *after* digestion in ammonia, &c., deducted from the weight of the calcined ore, indicates the amount of oxide of zinc dissolved out; and this, minus ¼ deducted for oxygen, indicates the amount of zinc present in the quantity of ore operated on.

Example:—

	Grains.	
Weight of blende taken	25	
Weight of calcined ore *before* treatment with ammonia, &c.	21·23	
Weight of calcined residue *after* treatment with ammonia, &c.	3·90	
Loss = Oxide of zinc, soluble in the ammoniacal solution	17·33	
Deduct ¼ for oxygen	3·46	
Zinc in 25 grs. of blende	13·87,	or 55·48 %

When the ore is finely powdered, and contains only a small proportion of foreign matter, there is no difficulty in extracting practically the whole of the oxide of zinc from the calcined ore by the direct action of ammonia and carbonate of ammonia. But when the amount of oxide of iron or earthy matter is large, a portion of the oxide of zinc will be retained in the residue. This especially occurs with oxide of iron, in which case it is better to modify the process thus:—After the ore is calcined it must be treated with hydrochloric and nitric acids, and to the solution, diluted with water, ammonia and carbonate of ammonia are added; the insoluble residue and the precipitate are collected together on a filter, washed, ignited, and weighed: the weight deducted from the weight of the calcined ore gives the quantity of oxide of zinc soluble in the ammoniacal solution. If the residue is now examined, it will be found to be practically free from zinc. Of course, if the ore contains silicate of zinc, the amount of oxide of zinc existing as such will be extracted at the same time; so that this modification cannot be resorted to if it is wished to determine the amount of zinc exclusive of that existing as silicate. Sometimes it is desirable to ascertain roughly for smelting purposes in an ore of zinc, how much zinc is present as silicate; and this may be done by means of the solvent action of ammonia and carbonate of ammonia on the calcined ore, when the silicate of zinc is left comparatively unacted upon; but the digestion should not be continued too long, otherwise the silicate will be attacked and zinc dissolved.

Examples of results actually obtained and relating to the preceding description.

1. 20 grs. of finely powdered blende (from Laxey, Isle of Man), nearly pure, after calcination over an air-gas-burner weighed 16·85: after digestion in a mixture of hot ammonia and carbonate of ammonia the ignited residue weighed 0·26 grs.

16·85 − 0·26 = 16·59 grs. of oxide of zinc dissolved out; 16·59 − 3·32 (oxygen) = 13·27 grs. of zinc; or 66·35 %.

The insoluble residue, after ignition, contained a trace of zinc, and the ammoniacal solution a trace of copper.

2. 25 grs. of calcined calamine (prepared for smelting) weighed after calcination 21·45 grs.: after digesting in ammonia and carbonate of ammonia, the ignited residue weighed 4·86 grs., and the ammoniacal solution was tinted slightly by copper.

21·45 − 4·86 = 16·59 grs. of oxide of zinc; 16·59 − 3·32 (oxygen) = 13·27 grs. of zinc; or 53·08 %.

The 4·86 grs. of residue, after prolonged re-digestion in ammonia and carbonate of ammonia, on re-ignition, weighed 4·75 grs. By boiling in hydrochloric acid, and estimating the zinc dissolved as oxide, the latter weighed 0·56 gr., which is equivalent to 1·78 % of zinc left in the insoluble residue. Three assays on the same sample of ore by the sulphide of sodium plan gave as a mean result 53·45 % of zinc.

3. 20 grs. of blende, containing 20·48 % of sulphide of iron (=13·03 % of iron), after calcination in a muffle, weighed 16·65 grs. The calcined product was digested with twice its weight of carbonate of ammonia, and some ammonia, for about ¾ of an hour; the insoluble residue, collected on a filter, and ignited, weighed 5·97 grs.; after re-digestion with ammonia, &c., it weighed 5·88 grs.

16·65 − 5·88 = 10·77 grs. of soluble oxide of zinc; equivalent to 8·61 grs. of zinc or 43·05 %.

The 5·88 grs. of residue, acted on by hydrochloric acid and then digested with ammonia and carbonate of ammonia, gave of insoluble matter, after washing on a filter and ignition, 4·28 grs. The filtrate contained zinc. 5·88 − 4·28 = 1·60 grs. of soluble matter, equivalent to 1·28 of zinc, or 6·40 %, retained in the first residue by the sesquioxide of iron, and not dissolved out by the direct action of the ammoniacal solution. 43·05 + 6·40 = 49·45 %; analysis gave 49·38 % of zinc. Another experimenter on the same ore obtained the following results:—By the direct action of ammonia and carbonate of ammonia on the calcined ore, 42·74 % of zinc. By treating the calcined ore with hydrochloric acid, boiling with ammonia, carbonate of ammonia, &c., and then weighing the insoluble residue, 50·38 % of zinc.

4. 50 grs. of calcined calamine (prepared for smelting), containing silicate of zinc, after calcination weighed 46·20 grs.; after treatment with ammonia and carbonate of ammonia, and igniting the insoluble residue, it weighed 19·05 grs.; equivalent to oxide of zinc dissolved, 27·15 grs.; equivalent to 21·72 grs. of zinc, or 43·44 %. The residue gelatinized on the addition of hydrochloric acid, and contained a considerable amount of zinc (about 11·35 %). Two assays by the sulphide of sodium plan gave 54·65 and 54·94 % of zinc; the mean of these results is = 54·79 %.

5. 20 grs. of finely-powdered native hydrated silicate of zinc, containing 53·33 % of zinc, were digested with a hot solution of ammonia and carbonate of ammonia five times successively, and the decanted solution was each time tested for the presence of zinc; about three-fourths of the oxide of zinc were extracted on the first digestion; a small quantity on the second and third; a very much smaller quantity on the fourth; and on the fifth a trace of zinc was still extracted. The final residue was decomposed by hydrochloric acid, and the zinc estimated as oxide, which weighed 0·22 grs.; equivalent to 1·10 % of zinc left insoluble after the action of the ammonia.

The following experiment was made to determine the amount of oxide of zinc which may be dissolved out of *calcined* silicate of zinc by a solution of ammonia and carbonate of ammonia: 20 grains of silicate were employed. By the 1st digestion, 26·15 % of oxide was extracted; by the 2nd, 4·15 %; and on further digestion zinc continued to be dissolved.

TABLE OF RESULTS OBTAINED BY DIFFERENT METHODS USED FOR ESTIMATING ZINC.

NATURE OF THE ORE.	Percentage of Zinc. I. By Analysis.	II. By a standard solution of sulphide of sodium.	III. By the solvent action of ammonia and carb. of ammonia.
1. Blende, from Laxey, nearly pure.....	..	66·54	66·3
2. Blende, containing sulphides of iron and manganese.....	49·38	49·78	49·5
3. Same sample as 2, by another person.....	..	49·3	50·4
4. Blende, with carbonate of lime, &c.....	54·93	55·25	..
5. Blende, with spathose iron ore, carbonate of lime, &c.....	39·44	39·33 39·56	..
6. Calcined calamine, containing silicate of zinc.....	..	53·61 53·71	..
7. Calcined calamine, containing copper.....	..	53·38 53·61	53·1
8. Same sample as 7, by another person.....	..	53·21 53·35	..

1. The same ore as that used in Experiment 1, p. 602.

2. The result in column 1 was obtained as follows: after the separation of the iron and manganese, the zinc was precipitated as sulphide, which was redissolved in acid, and from the solution thus obtained, it was precipitated as carbonate and after ignition weighed as oxide.

3. In column 3 the result was obtained by a modification of the ammonia plan, *i. e.* by decomposing the ore with acid before dissolving the oxide of zinc.

4. In column 1 the result was obtained by weighing the zinc as oxide.

5. In column 1 the result was obtained by evaporating the ammoniacal filtrate to dryness, and afterwards precipitating the zinc by carbonate of soda, and weighing as oxide of zinc.

7. In column 2 the result was obtained as follows: the copper was precipitated from the hot ammoniacal solution by sulphide of sodium, the solution filtered, and the zinc determined in the filtrate when cold. The same ore was used in Experiment 2, p. 602.[1]

By a standard solution of bichromate of potash, &c.—This process depends upon the fact that a solution of sesquichloride of iron is reduced to the state of protochloride, by freshly precipitated sulphide of zinc, with the liberation of sulphur: this reaction is explained by the formula

$$Fe^2Cl^3 + ZnS = ZnCl + S + 2FeCl.$$

The amount of protochloride of iron formed is afterwards estimated by a standard solution of bichromate of potash or permanganate of potash, as in the wet method of assaying iron ores.

The bichromate of potash solution employed for estimating iron is made by dissolving about 305 grs. of the crystals in 4 pints of water, and this may also be used in the assaying of zinc ores. But if it is prepared specially for the purpose, it should be made stronger, in order to obviate the necessity which may sometimes arise of refilling the

[1] 1. By R. Smith. 2. By R. Smith. 4. I By C. Tookey. II. By R. Smith. 5. I. By C. Tookey. II. By R. Smith. 7. By R. Smith.

burette during the process, viz. by dissolving 525 grs. of the bichromate in 4 pints of water; 200 divisions (1000 grs.) of this solution will indicate about 17·2 grs. of iron, or be equivalent to about 10 grs. of zinc. The solution of ferricyanide of potassium, used in conjunction with the bichromate, is prepared by dissolving 2 grs. of the crystals in about 8 fluid ounces of water.

The strength of the solution of bichromate of potash may be determined by dissolving in a flask a known weight of pure iron wire (from 5 to 10 grs.) in hot dilute hydrochloric acid, diluting the colourless solution with about ½ a pint of water, and adding the bichromate, until a drop of the solution taken out ceases to give the faintest trace of blue colour with a drop of the ferricyanide of potassium solution: every 10 grs. of iron present will be equivalent to 5·81 grs. of zinc. Full details will be given concerning this process, under the subject of Iron, in a subsequent volume.

Process.—A known weight of the ore is to be taken, and the ammoniacal solution of zinc obtained in the same way as in the sulphide of sodium plan. To the warm ammoniacal solution, sulphide of sodium or sulphide of ammonium in slight excess is added, the precipitated sulphide of zinc is collected on a filter, and washed with warm ammoniacal water. The filter with its contents is transferred to a beaker-glass provided with a glass cover, and after the addition of an excess of a slightly acid, dilute solution of sesquichloride of iron, the whole is digested at a gentle heat for about 10 or 15 minutes; sulphuric acid is then poured in; a gentle heat is continued to be applied until the sulphur coagulates; the solution is filtered and the filter washed with warm water, after which the amount of protochloride of iron present in the filtrate is determined by bichromate of potash as follows:—The filtrate, if necessary, is diluted with water to about ¾ of a pint, and a small quantity of hydrochloric acid is added: the standard solution of bichromate of potash is then gradually added, until all the iron is converted into sesquichloride, and a drop of the solution taken out on the end of a glass rod ceases to give the slightest trace of blue colour, with a solution of ferricyanide of potassium (red prussiate of potash) previously dotted out on a white porcelain slab or plate. The number of divisions of the bichromate of potash used is then read off, and from the quantity of iron present as protochloride the amount of zinc is calculated; 56 parts of iron will be equivalent to 32·53 of zinc. For example:—200 divisions (1000 grs.) of the bichromate indicate 10 of iron, or 5·81 of zinc.

Iron.		Iron.		Zinc.		Zinc.
56	:	10	:	32·53	:	5·81

20 grs. of the zinc ore required 180 divisions of the bichromate of potash.

Divisions.		Divisions.		Zinc.		Zinc.
200	:	180	:	5·81	:	5·23

$5{\cdot}23 \times 5 = 26{\cdot}15\ \%$ of zinc.

The above process yields good results; but that by a standard solution of sulphide of sodium is to be preferred for practical purposes on the ground of rapidity of execution.

BRASS.[1]

In this work the term brass will be restricted to alloys consisting essentially of copper and zinc; but it should be more properly confined to such as are either decidedly yellow or have the yellowish tint characteristic of brass. The old English name for it is *latten*. Copper and zinc unite in all proportions and form homogeneous alloys, and the union is attended with the evolution of heat. The number of these alloys in actual use is considerable. There is great confusion with respect to the names by which they are distinguished; for in some cases different terms are applied to the same alloy, and in others the same terms are applied to different alloys. Thus the terms *tombac*, *prince's metal*, *similor*, and *Mannheim gold* are used by some authors to designate alloys consisting of about 85 per cent. of copper and 15 per cent. of zinc; whereas, according to other authors, *prince's metal* and *Mannheim gold* are synonymous, and are composed of 75 per cent. of copper and 25 of zinc;[2] according to another author *similor* consists of about 71½ per cent. of copper and 28½ per cent. of zinc, and *Mannheim gold* of 80 per cent. of copper and 20 per cent. of zinc;[3] and, again, according to another author, *similor* and *Mannheim gold* are synonymous, and are applied to alloys of copper containing from 10 to 12 per cent. of zinc and from 6 to 8 per cent. of tin.[4] Seeing that such inextricable confusion exists in the employment of the terms above mentioned, it is desirable to discard them altogether, and to indicate the varieties of brass by their per-centage composition. But when the term brass is used without qualification, it is generally intended to indicate an alloy consisting of about 2 parts by weight of copper and 1 of zinc.

Birmingham is the principal seat of what may be termed the brass industry of this country. It is stated that the trade was introduced into the town, about A.D. 1740, by the family of Turner, and that the chief supply of the metal was derived from the Macclesfield, Cheadle, and Bristol Companies.[5]

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[1] In a subsequent part of this work I shall examine the subject of the *constitution* of alloys; and I adopt this plan because an extensive knowledge of alloys is essential for such an examination, and I think it will be most agreeable and instructive to the reader to acquire it gradually in the consecutive study of the various metals.

[2] Supplement to Ure's Dict. of Arts, &c., 1844, p. 35; Gmelin's Handbook, loc. cit.

[3] Handbuch der Metall-Legirungen, von Joh. Tenner. Quedlinburg, 1860, p. 15.

[4] Regnault, Cours élémen. de Chimie, 2ième éd. 3. p. 300.

[5] Hutton's History of Birmingham, 1795, p. 113.

It appears that the manufacture of brass was for some time in the hands of a few wealthy persons in Birmingham, who acted, as monopolists usually act, in an impolitic manner, and overreached themselves. Upon this subject I may introduce the following somewhat quaint observations of Hutton, the historian of Birmingham. These monopolists, "instead of making the humble bow for favours received, acted with despotic sovereignty, established their own laws, chose their own customers, directed the price, and governed the market. In 1780 the article rose, either through caprice or necessity, perhaps the *former*, from 72*l.* a ton to 84*l.*; the result was an advance upon the goods manufactured, followed by a number of counter-orders and a stagnation of business. In 1781, a person, from affection to the user, or resentment to the maker, perhaps the *latter*, harangued the public in the weekly papers, censured the arbitrary measures of the brazen sovereigns, showed their dangerous influence over the trades of the town, and the easy manner in which works of our own might be constructed. Good often arises out of evil: this fiery match, dipped in brimstone, quickly kindled another furnace in Birmingham. Public meetings were advertised, a committee appointed, and subscriptions opened to fill two hundred shares of 100*l.* each, deemed a sufficient capital; each proprietor of a share to purchase one ton of brass annually. Works were immediately erected on the banks of the canal, for the advantage of water-carriage, and the whole was conducted with the true spirit of Birmingham freedom. The old companies, which we may justly consider the directors of a South Sea bubble in miniature, sunk the price from 84*l.* to 56*l.* Two inferences arise from this measure: that their profits were once very high, or were now very low; and, like some former monarchs in the abuse of power, they repented one day too late."[6] The new works were those to which reference will hereafter be made as belonging to Mr. Pemberton. In 1795 the annual consumption of brass, according to Hutton, in Birmingham amounted to 1000 tons.

The qualities which render brass so valuable may be succinctly stated as follows:—It is harder than copper, and therefore better resists wear: it is malleable and ductile in a high degree, so that it may be rolled into thin sheet—shaped into vessels of various kinds by means of the hammer—raised by the process of stamping into objects such as curtain-bands—and drawn out into fine wire: it is well adapted to casting, as it is easily fusible—at a lower temperature than copper—and is capable of receiving very delicate impressions from the mould: it is stated to resist atmospheric influences better than copper; but when its surface is unprotected by lacquer, it rapidly tarnishes and becomes black; it has a pleasing colour, and is susceptible of a fine polish; and, lastly, it has one great advantage over copper, namely, cheapness. The so-called *Dutch metal*, or *leaf*, furnishes an excellent illustration of the remarkable malleability of certain kinds of brass: it is only brass containing a large proportion of copper, and is made

[6] Op. cit., pp. 114, 115.

by beating out the laminated metal in the same manner as gold-leaf; the thickness of the leaves of Dutch metal is stated not to exceed $\frac{1}{32500}$ inch.

The malleability of brass varies with its composition and with the temperature; and it is also affected, in a very decided degree, by various foreign metals, though present only in minute quantities. Some kinds of brass are malleable only while cold, others only while hot, and others are not malleable at any temperature. At a temperature sensibly below fusion, all brass, like copper, is brittle, and may be reduced by trituration to powder. When an ingot of brass is broken while hot, its fracture is coarsely fibrous or columnar; but when broken cold, it should be finely granular; at least in the case of certain descriptions. According to Berthier, zinc is never completely volatilized from copper by heat.[7] A table will be found further on containing information concerning the working qualities, colours, &c., of numerous alloys of copper and zinc.

When the fracture of a *cast* ingot of certain metals is fibrous, the directions of the fibres will generally be at right angles to the cooling surfaces. In the case of a sphere, the fibres will have the direction of radii; and in the case of a square or rectangular prism, two diagonals will be plainly visible on the transverse fracture, formed by the points of junction of the internal extremities of the fibres. I have excellent illustrations of such arrangements of fibres.

According to Storer, "the tendency to shoot into fibres . . . extends over quite a space, from alloys containing 57 or 58 per cent. of copper, or even more, down to those containing 43 or 44 per cent., where it gradually disappears. . . . It is remarkable that this inclination to form fibres is strongest in those alloys which contain nearly equal equivalents of zinc and copper, being less clearly marked as one recedes in either direction from this point, until a stringy texture analogous to that of copper is reached on the one hand, and the peculiar pastiness of zinc on the other. In preparing crystals, this pastiness manifests itself decidedly in the alloys immediately below those which are fibrous, becoming more strongly marked as the alloys are richer in zinc; at least so far as my own observations have extended, *i. e.* to 30 per cent. or less of copper. The fracture of these white alloys is for the most part vitreous."[8] I have ingots of best-selected copper, cast in closed iron moulds, which have *not a stringy*, but a *coarsely fibrous* transverse fracture: these ingots are 12 inches long, and exactly 1 inch square, and the fracture was obtained by breaking them while *cold*. On attempting to roll them, either cold or hot, and with a very gently graduated pressure, they were cracked in innumerable places.

There is great variation in colour in the alloys of copper and zinc, from the red of copper at one extreme to the bluish white of zinc at the other. The transition from one to the other is gradual, through intermediate stages of yellow.

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[7] Tr. des Essais, 2. p. 603.

[8] On the Alloys of Copper and Zinc, by Frank H. Storer; Memoirs of the American Academy, 1860, 8. p. 35.

By fusion, brass is occasionally obtained in tolerably good crystals. During at least twelve years I have had such crystals in my possession, and they have always appeared to me to resemble the regular octahedron; but unfortunately they are not sufficiently perfect to admit of admeasurement; and without this no positive statement of any scientific value can be made on the subject.

Numerous experiments have been made by Mr. Storer, Harvard College, U. S., on the production of crystals of various kinds of brass, by the usual method of preparing crystals of bismuth; and the conclusion at which he has arrived is, that the crystals of brass are octahedrons belonging to the monometric or cubical system, and that zinc is isomorphous with copper, which, as is well known, crystallizes in that system. He obtained the most perfect individual crystals from a quantity of brazier's solder, which consists of equal parts, by weight, of copper and zinc, and occurs in the state of coarse powder, produced by heating the alloy to a sufficient degree, and triturating it while hot. Mr. Storer adduces, in support of his conclusion that zinc belongs to the monometric system, the statement of Nicklès, that this observer obtained zinc in the form of pentagonal dodecahedrons; and he suggests that surely Nicklès could not be mistaken on a point of crystalline form, though the eminent crystallographer, Gustav Rose, who doubts the statement of Nicklès, might be mistaken. We have obtained crystals of zinc in small spherical aggregations, which, as far as a judgment can be formed from description, appear to be identical with those described by Nicklès. They are now in the possession of Professor Miller of Cambridge, who will probably be able to decide the point in question, and who will, if I mistake not, pronounce a judgment in favour of Rose.

During the process of stamping brass—that is, of subjecting it to heavy blows in dies, as is done in the manufacture of various articles used in modern decoration—it is requisite to anneal the metal from time to time. After the completion of the stamping, the article will remain discoloured with adherent oxide formed in the annealing process. This is easily detached by plunging the metal in *aquafortis* of suitable strength, and then washing with water. A bright metallic surface is thus produced, ready to receive the usual coating of varnish or lacquer. This process of cleansing the surface is known by the name of "dipping." If the brass contains certain impurities, it will not "dip"—that is, it cannot be made to acquire a bright surface by the application of acid. The colour produced by dipping may be varied by the use of *aquafortis* (nitric acid) of different strengths. This, I presume, will depend upon the component metals being dissolved in different ratios by acids of varying strength. An alloy consisting of about 95 per cent. of copper, and 5, or somewhat less, of aluminium, acquires, by suitable "dipping" in nitric acid, a colour so closely resembling that of fine gold, that I think it scarcely possible to distinguish one from the other, even when seen side by side. We ascertained this fact several years ago in the Metallurgical Laboratory; and I have frequently mentioned it in public, and exhi-

bited illustrative specimens of it; yet I do not find that it has received any attention. Unfortunately the beautiful gold-coloured surface thus produced tarnishes, and can only be preserved by a covering of varnish or lacquer. The process called "dead-dipping" is extensively practised in Birmingham, where I understand it was introduced not many years ago. I saw it practised (Oct. 1854) in the following manner at large brass-works, where it was accidentally discovered:—

Dead-dipping.—This term is applied to the process of producing an agreeable pale yellow dead surface on brass works, such as curtain bands, &c. The brass work, with the adherent black scale produced in annealing after the final stamping, is "pickled" in dilute nitric acid or aqua fortis (say 1 part of acid to 7 or 8 parts of water): the precise strength is not particularly attended to; acid which has been employed in the subsequent part of the process being put aside for the purpose. It is left in this acid "pickle" until the scale may be easily detached by gently rubbing the surface with the finger. It is then taken out and immediately washed by moving it about in water; after which it is put into much stronger acid, and left in it until the surface of the metal becomes white with "curd," an appearance which is due to a stratum of small bubbles of gas uniformly diffused over the surface. No precaution is taken to ensure the use of acid of constant strength: it may be about twice as strong as that used in the first step of the process, or may consist of about 1 part by measure of acid and 4 of water. I saw several pieces of stamped work fastened or strung together by a piece of brass wire, and treated as above described; I was informed, however, that each piece ought to be dipped separately, but that the workmen would be thus careless and operate upon several pieces at a time in spite of every effort to prevent their doing so. As soon as the white stratum or "curd" has properly formed, the brass is washed in water and then roughly dried by moving it about in *cold* sawdust. It is next dipped, with adherent particles of sawdust, in *strong* nitric acid for a few seconds, washed in water, and immediately afterwards washed again in water, *not heated*, containing argol or impure cream of tartar dissolved, which done, it is dried in *hot* sawdust. The argol solution is said to prevent a brownish discoloration or mottling of the surface which would otherwise occur. This mottling, moreover, is produced if the drying sawdust is not hot enough. The sawdust is kept heated in a large quadrangular iron pan, placed upon a suitable brick stove. Although the workmen are in the habit of subjecting several pieces of work together to the *first* and *second* dippings, yet, in every case, in the *last* each piece must be dipped separately. The dipped surface is now ready for lacquering.

By casting copper, heated to a certain temperature, *under* water, I have obtained an ingot coloured superficially so exactly like brass that any one would mistake it for this alloy.

1.	2. Atomic Constitution.	3. Composition per cent.	4. Specific Gravity.	5. Colour.	6. Order of Intensity of Colour.	7. Fracture.	8. Cohesive Power per sq. inch in Tons.	REMARKS.
1	Cu	100	8·667	..	..	..	24·6	6. Approaching *tombac* in colour; is not quite so good for rolling, hammering, or wire-drawing as common "red-brass," which contains less copper in proportion to the zinc.
2	10 Cu + Zn ..	90·70+ 9·30	8·605	Reddish yellow	1	C. C.	12·1	8. Comes very near "red-brass," which it quite equals with respect to its working qualities.
3	9 Cu + Zn ..	89·80+10·20	8·607	Reddish yellow	2	F. C.	11·5	10. The reddish colour is now beginning to pass into brass-yellow; "behaves itself irreproachably" under the rolls and hammer, and in wire-drawing.
4	8 Cu + Zn ..	88·60+11·40	8·633	Reddish yellow	3	F. C.	12·8	13. Working qualities quite the same as those of common brass. Karsten remarks that it was this alloy which was puffed for some time in England under the name of mosaic gold.
5	7 Cu + Zn ..	87·30+12·70	8·587	Reddish yellow.....	4	F. C.	13·2	14. In working qualities not different from common brass.
6	.. ..	*86·3 +13·7	8·7055	..	..	..	..	16. It contains 4 per cent. more zinc and 4 per cent. less copper than common brass. The colour is no longer pure brass-yellow, but has a reddish tinge; works excellently under the rolls and hammer, as well as in wire-drawing.
7	6 Cu + Zn ..	85·40+14·60	8·591	Yellowish red	3	F. F.	14·1	19. Much to be recommended on account of its golden colour, though it possesses greater tenacity, but less hardness, and is brittle. Well adapted for cast ware. Very flexible after casting while still hot. When cold is hard to cut, and is rather fractured than cut. The ingots, after being cut, annealed, and cooled, can no longer be rolled. If, after heating and cooling to the temperature of boiling water, they are rolled, it produces only very brittle, fragile sheets, much cracked at the edges, notwithstanding frequent annealing during rolling may have been resorted to: it is quite unsuitable for rolling, hammering, or wire-drawing.
8	.. ..	*84·0 +16·0	8·6390	..	..	..	..	
9	5 Cu + Zn ..	83·02+16·98	8·415	Yellowish red	2	F. C.	13·7	
10	.. ..	*80·6 +19·4	8·6796	Yellowish red	..	..	..	
11	4 Cu + Zn ..	79·65+20·35	8·448	Yellowish red	1	F. C.	14·7	
12	.. ..	*75·9 +24·1	8·6095	Brass-yellow	..	..	..	
13	3 Cu + Zn ..	74·58+25·42	8·397	Pale yellow	..	F. C.	13·1	
14	.. ..	*73·8 +26·2	8·5821	Brass-yellow	..	..	..	
15	.. ..	*67·5 +32·3	8·4996	Reddish brass-yellow.	..	..	..	
16	2 Cu + Zn ..	66·18+33·82	8·299	Full yellow	1	F. C.	12·5	20. Very flexible while strongly heated. Rolls tolerably well cold, though it frequently cracks at the edges. During rolling into thin sheets, it requires more frequent annealing than common brass. Cannot be soldered, as it melts at the same temperature as the solder. Not adapted for wire-drawing.
17	.. ..	60·0 +40 0·	..	Yellow	..	..	..	
18	.. ..	*59·0 +41·0	8·3751	Reddish yellow... ..	..	..	..	
19	.. ..	*52·0 +48·0	8·2292	Nearly gold yellow ..	..	..	..	
20	Cu + Zn ..	49·47+50·53	8·230	Full yellow	2	C. C.	9·2	21. Fracture reticulated. Possesses a tolerable degree of tenacity, but by hammering becomes so brittle that at no temperature can it be sufficiently drawn out for practical purposes.
21	.. ..	*46·5 +53·5	..	Reddish white.....	..	..	..	
22	.. ..	*44·0 +56·0	..	White, but viewed obliquely, deep yellow.	..	..	..	
23	.. ..	*35·5 +64·5	..	Bluish white	..	..	..	22. Lustre is so imperfectly metallic, that it would hardly be recognized as a metallic alloy. Its great brittleness and frangibility, combined with its perfectly conchoidal and smooth fracture, communicate to the alloy more the appearance of a sulphur compound than that of a mixture of two metals.
24	Cu + 2 Zn	32·85+67·15	8·283	Deep yellow.....	..	C. C.	19·3	
25	8 Cu + 17 Zn	31·52+68·48	7·721	Silver-white (?)	1	C.	2·1	
26	8 Cu + 18 Zn	30·30+69·70	7·836	Silver-white (?).....	2	V. C.	2·2	
27	8 Cu + 19 Zn	29·17+70·83	8·019	Silver-grey.....	3	C.	0·7	23. More brittle than the last; fracture smooth, even, small-conchoidal; lustre strongly metallic.
28	8 Cu + 20 Zn	28·12+71·88	7·603	Ash-grey	3	V.	3·2	
29	8 Cu + 21 Zn	27·10+72·90	8·058	Silver-grey.....	2	C.	0·9	25, 26, 27. Very brittle. Too hard to file or turn; lustre nearly equal to that of Speculum Metal.
30	8 Cu + 22 Zn	26·21+73·76	7·882	Silver-grey.....	1	C.	0·8	
31	8 Cu + 23 Zn	25·39+74·61	7·443	Ash-grey	4	F. C.	5 9	28, 29. Brittle. Ditto ditto ditto.
32	.. ..	*24·8 +75 2	..	Bright lead-grey.....	..	..	..	30. Very brittle. Ditto ditto ditto.
33	Cu + 3 Zn	24·50+75·50	7·449	Ash-grey	1	F. C.	3·1	31. Barely malleable.
34	.. ..	*21·0 +79·0	..	Bright lead-grey	..	..	..	32. Brittle; fracture granular, uneven: has a tolerable degree of tenacity, but cannot be worked under the rolls or hammer.
35	Cu + 4 Zn	19·65+80·35	7·371	Ash-grey	2	F. C.	1·9	33. Brittle.
36	Cu + 5 Zn	16·36+83·64	6·605	Very dark grey	..	F. C.	1·8	34. In external characters and working qualities, closely resembles No. 32.
37	.. ..	*14·7 +85·3	..	Much resembling No.32	..	..	..	36. Brittle. 38. Fracture finely granular.
38	.. ..	*11·25+88·75	..	..	..	..	..	39. Has sufficient tenacity to admit of being somewhat extended under the rolls and hammer, if, after annealing, it is not allowed to become quite cold.
39	.. ..	* 9 5 +90·5	..	Dark lead-grey	..	..	..	
40	Zn	100·0	6·895	..	..	..	15·2	

[1] Report of the Meeting of the British Association at Glasgow in 1839.

[2] Archiv. 1839, 12. p. 385.

Note.—Those marked (*) are by Karsten. The numbers in column No. 6 denote intensity of tint of the same colour. The letters in column No. 7 are abbreviations for the characters of the fractures according to Mr. Mallet's nomenclature, thus: F. F., fine-fibrous. C., conchoidal. V. C., vitreo-conchoidal. V., vitreous. F. C., fine-crystalline. C. C., coarse crystalline. The cohesive power was determined on prisms 0·25 inch square, without having been hammered or compressed after being cast. The weights given are those which each prism just sustained for a few seconds before disruption.

Observations on the preceding Table.—The alloys employed by Mr. Mallet were made in a closed, bent, wrought-iron tube, coated and lined with porcelain clay and plumbago. The zinc was gradually brought in contact with the copper: the apparatus excluded air, and was continually agitated, until the alloy was poured into a mould of cast-iron, into which it was cast into a long strip, which solidified instantly. About 7 lbs. weight of each alloy were formed at once; and the constitution of each, where any cause of doubt existed, was verified afterwards by an assay.

Mr. Mallet states that the addition of only $\frac{1}{8}$ of an equivalent of zinc to the yellow and tough alloy, 2Zn+Cu, renders it white and extremely brittle.

It will be found that the specific gravities of the alloys do not increase in regular proportion to the amount of copper which they contain, though their general tendency is to do so: the greatest disturbances occur in the series from 8Cu+17 Zn to 8Cu+23Zn.

The specific gravities were taken on the alloys just as they were cast, and suddenly cooled in the cast-iron mould; but it was found that on rolling some of them condensation took place in very variable degrees, from which Mr. Mallet infers that sudden cooling produces an effect on the alloys of copper and zinc analogous to *tempering* in cold water.

PREPARATION OF BRASS.

Until a comparatively recent period all brass was made by the old process of *cementation*, which has been almost entirely superseded by that of alloying zinc in the *metallic* state directly with copper. This ancient process, which had been practised for centuries, was, nevertheless, patented in this country in 1779, by Mr. John Champion, senior![9]

Manufacture of Calamine Brass.

Only a few years ago I saw the old process carried on in Birmingham at Mr. Pemberton's works, the last which survived in that town; but they have since been pulled down, and I am not aware whether a single calamine brass furnace is now in operation in England. In 1859 I found several of these furnaces still in existence at the copper-works of Messrs. Sims, Nevill, and Company, at Llanelly, Glamorganshire, and there are others, I am informed, at Swansea. I am indebted to the kindness of the firm just mentioned for permission to examine them, and take the measurements from which the accompanying wood-cuts have been prepared. I have also pleasure in stating that I received much of the following information concerning the mode of conducting the process from the late Mr. Joseph Stringer, who had been during a long period in their employ, and who had superintended the furnaces.

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[9] A.D. 1779, Nov. 24. No. 1239. Abridgments—Metals and Alloys, p. 22.

Description of the furnace.—It exactly resembles, in all essential points, the furnaces represented in the engravings contained in old metallurgical treatises. It consists of a circular chamber *m*, lined with firebrick, *d d*; it is contracted above to a circular opening, the mouth, in which is fixed a cast-iron collar, *e e*; it is closed at the bottom by a circular cast-iron plate or bed-plate, *a a*, in which are 12 holes sym-

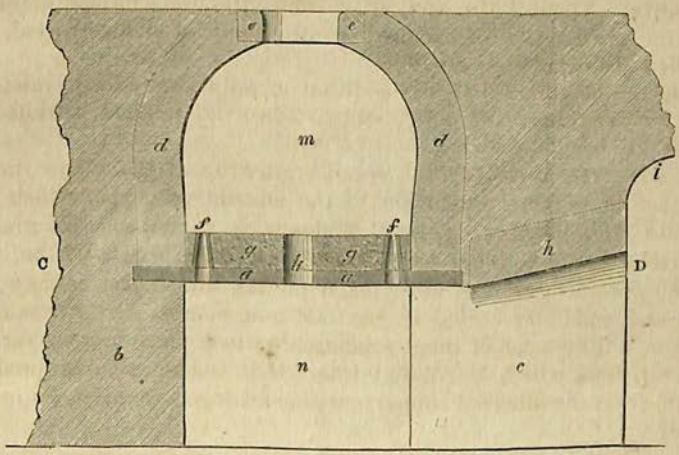

Fig. 151. Vertical Section on the line A B, fig. 152.

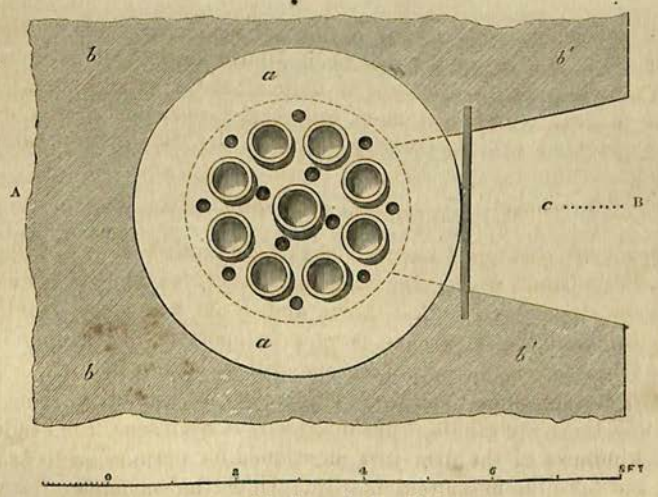

Fig. 152. Horizontal Section on the line C D, fig. 151.

metrically arranged round one larger hole in the centre, *k*, through which the ashes and clinkers may be withdrawn from time to time; below the bed-plate is the ash pit, *n*, communicating in front by means of an arched air-way, *c*, with a long arched passage or vault, *i*, through which air is conveyed to the furnace from the outside, and the workmen obtain access to the ash pit. Over the small holes in the bed-plate are

placed short nozzles or twyers of cast-iron, *f f*, tapering upwards, the larger central hole being left without a nozzle. The nozzles are 6 inches high, 2½ inches in diameter at the bottom, and 1 inch at the top, inside measure, and ¾ inch in thickness. The space between the nozzles is filled up level with bricks and fire-clay, so as to form a solid bed 6 inches thick. The air which sustains combustion enters through these nozzles, which are used as a substitute for bars. The furnace is enclosed in a solid mass of brick-work, *b b*; and for the sake of strength, at the back of the arch, *h*, over the air-way, *c*, and in front of the bed-plate, is placed an iron bar resting upon the walls, *b' b'*, which form the sides of this air-way. Several of these furnaces are constructed in a row, and over the whole is built a room of brick covered in with a large brick cone, open at the top, exactly like an ordinary glass-house.[1] It will be perceived that the furnace has no chimney, except the mouth, which is kept more or less closed, according to circumstances, by a circular cover of cast-iron, or of fire-brick set in an iron frame. In the accompanying woodcuts, the furnace is shown as widening somewhat to the height of 13 inches above the upper surface of the bed-plate. The furnace-builder, whom I interrogated, stated that it did not thus widen upwards, but Mr. Stringer stoutly maintained that it did; and I could not succeed in determining this point for myself, which is not very material.

Crucibles.—The crucibles employed are made of fire-clay. They are circular, and 12½ in. deep, 8¼ in. wide at the top, and 6¾ in. in the middle, inside measure; they are 1 in. thick at the top, and 2 in. thick at the bottom. Mr. Stringer informed me that he was always accustomed to employ a slightly larger crucible, which he termed the *king-pot*, in the centre of the bed-plate; but another calamine-brass maker of great experience tells me that there is no necessity for this variation in the size of the crucibles. According to Mr. Stringer, the *king-pot* should be 13½ in. deep, 8½ in. wide at the top, and 7¾ in. wide in the middle; 1¼ in. thick at the top and 2 in. thick at the bottom. Such a crucible will hold 120 lbs. of metal, while one of the smaller size will only hold 84 lbs.

Composition of the charge.—Calcined calamine or blende calcined *sweet* and ground fine, 100 lbs., ground coal 40 lbs. These are intimately mixed *dry*, and passed through a sieve of 8 holes to the linear inch. The mixture is then spread level, and 2 gallons of water are poured upon it; after standing half an hour, it is again well mixed and passed through a sieve of 4 holes to the linear inch, after which it is levelled and thoroughly mixed with 66 lbs. of *bean-shot* copper. The mixture should be sufficiently moist to adhere together by pressure with the hand. It is now ready for charging, and produces brass for the *best battery* purposes, *i.e.* brass intended for hammering, &c.

Mode of charging.—It is supposed that the furnace has become previously heated in the regular course of working. The pots are charged with care moderately lightly, covered, and arranged in the manner

[1] See description of the English Zinc Furnace, p. 553.

shown in fig. 152; the central hole in the bed-plate having been previously stopped with clay. Four flat pieces of coal, each about 15 in. long, from 3 to 4 in. thick, and 8 or 9 in. wide, are placed so as to form a cross over the pots, one end of each piece resting on a side-pot and the other on the king-pot. 3 cwt. of coal broken in pieces a little larger than the fist are then carefully put into the furnace, the fall of the coal being broken by placing a pair of tongs in the mouth, which is afterwards partially closed. The coal is thus left to burn until "all the gas is out of it," which will require about 1½ hour, when the cover is placed over the mouth to within ½ in. on one side in order "to harden the coke" formed. After this, the coked coal is cautiously poked down amongst the pots, care being taken to keep the draught holes open and clear. The cover is now placed to within 1½ in. on one side of the mouth, and the furnace may then be left during 3 hours without a further supply of coal. It is the duty of the foreman to see that the draught holes are properly cleared and the pots kept covered with coke. The heat is gradually raised in the course of the process by removing the cover a little on one side. The process, if properly attended to, will be completed in about 10 hours.

The brass which has been formed is now to be collected. The king-pot is taken out and its contents are well stirred with an iron bar having a flat or paddle-end. One of the side-pots is next taken out and treated in the same manner, when the brass, which has subsided to the bottom, is poured into the king-pot. The other side-pots are taken out in succession, and the same process repeated with each. The king-pot is well shaken with the stirring-bar during the pouring. The brass from all the side-pots having been thus collected in the king-pot, the metal in the latter is skimmed and poured into iron ingot moulds. It is scarcely necessary to remark, that as soon as a side-pot has been deprived of its brass, it should be replaced while hot in the furnace. An old calamine brass-maker informs me that good pots lasted on an average 16 days, not being allowed to cool during that period.

When brass of inferior quality is to be made, the weight of the copper in the charge above stated is reduced 1 lb., and spelter is added until the desired quality is attained. The spelter should be broken in small pieces and put into the bottom of the pot before charging with the regular mixture.

It is important in the manufacture of calamine brass, that the king or receiving pot should always be the cleanest, and have as little matter adhering to its sides as possible. The paddle is pushed down round the sides, so as to get the metal together, which cannot well be done if there is much concretionary matter round the inside; and by gently bumping the bottoms of the pots on the floor, the subsidence of the metal is promoted.[2]

[2] I may mention that, notwithstanding the incessant care which a calamine brass furnace requires, as it is kept in operation during long periods without intermission, the occupation does not appear to be injurious to health. I knew an old

The following details relate to Mr. Pemberton's calamine-brass-works formerly in operation at Birmingham. The diameter of a furnace was 3 feet 6 inches at the bottom, and the height 3 feet 6 inches to the collar. Stourbridge clay crucibles were employed, 12 inches deep and 8¼ inches in diameter. Each furnace contained 9 such crucibles. In later times only two qualities of brass were made, which were distinguished by the marks B. I. and B. XX. The charges were as follows:

	B. I. lbs.	B. XX. lbs.
Feathered-shot copper	64	61
Ground and sifted calcined calamine from Somersetshire	88 bushel.	97 bushel.
Coal-slack	1	1

Cost of making calamine-brass in the last century.—The following details, extracted from Mr. Morris's Journals previously referred to, may now be interesting to brass-makers for the sake of comparison:—

Brass House Calculation in 1781 (at the Forest Works).

Dr. cwt. qrs. lbs.	£.	s.	d.
9 1 20 Copper shot at £86 per ton	40	10	10
14 0 16 Calamine at £6 per ton	4	4	10
2½ bags of charcoal-dust at 30s. per dozen	0	6	3
33 bags of coal at 35s. per wey	0	15	4
Jno. Spears' week's wages	0	15	0
His brother do.	0	12	0
Helper	0	6	0
Wear of furnaces, tools, grinding and dressing calamine, charcoal, fern, &c.	0	7	6
	47	17	9
If copper at £96 per ton, add	4	14	3
	52	12	0
If the brass is made richer by using 6 lbs. more copper every charge	5	14	4
	£58	6	4

Cr. cwt. qrs. lbs.	£.	s.	d.
By 14 0 16 Brass at £90 per ton	63	12	10
10 lbs. of do. in skimmings at £45 per ton	0	4	0
	£63	16	6

The copper is estimated to increase 50 per cent. in weight; and the brass, which is composed of 2 parts of copper and 1 of zinc, to be equal to the weight of the calamine used.

---

calamine brass furnace-man at Mr. Pemberton's works who had been constantly employed in the business during sixty years, having commenced when a boy ten years old. He had scarcely had one continuous night's rest out of five nights every week during that long period, and yet he appeared vigorous, and by no means unhappy.

THE BRASS HOUSE CALCULATION IN 1784.

Dr. cwt. qrs. lbs.	£.	s.	d.	cwt. qrs. lbs.	Cr. £.	s.	d.
14 2 26 Copper shot at £80 per ton	58	18	7	By 22 0 11 brass at 65s. per cwt.	71	16	4
22 0 11 Calamine at £5 15s. per ton	6	7	1				
12 bags of charcoal at 30s. per dozen	1	10	0				
¾ wey of coal at 35s. per wey	1	6	3				
Workmen's wages	1	4	0				
Wear of furnaces, tools, grinding and dressing calamine, fern, &c.	1	3	0				
	70	8	11				
Profit	1	7	5				
The furnaces in one week	£71	16	4				

In this process oxide of zinc is reduced at a temperature below the melting-point of copper, which, being thus exposed to the action of the vapour of zinc, becomes permeated with this metal and converted into brass. Care must be taken so to regulate the temperature that the *copper shall not melt*, but remain diffused through the mass of the charge; for if it were allowed to melt, it would trickle down to the bottom of the pot, in a greater or less degree, and much of the zinc would then escape.

By exposure to the vapour of zinc, copper may be converted into brass even below the melting-point of this alloy. In illustration of this fact, the following pretty experiment may readily be made:—A little zinc is placed at the bottom of a clay crucible, and covered with a layer of coarsely-pounded fire-brick or burnt fire-clay; a copper coin is then introduced and surrounded with coarse charcoal-powder; after which the crucible is closed with a luted cover, and exposed during a considerable time to a gentle red-heat. The surface of the coin will by this means be converted into yellow brass, without obliterating the effigy and other characters upon it. In experiments of this kind which we have made, the surface has always had a crystalline or *frosted* appearance.

Calamine-brass was formerly used by button-makers in the manufacture of *gilt buttons*, which were gilt by the old process of *water-gilding*, *i. e.* by means of mercury (*lucus a non*, &c.)—a designation which would be more appropriate to the modern method of electro-plating. It was preferred for this purpose, because it was said to receive the gold better than brass made from spelter; and to "stand the soldering better," to which these buttons were subjected in attaching the shanks. It was also specially used in making the wire-gauze employed in the sieves of papermakers. A thoroughly practised brass-worker in Birmingham most positively maintains to me that he can immediately distinguish calamine-brass from common brass by the peculiar appearance of its polished surface. Why calamine-brass should differ from common brass, I do not at present understand; but that such a difference actually existed when the former kind of brass was largely produced, can hardly be denied. Indeed so impressed are some of the Birmingham

brass-founders with the fact of this difference, that quite recently I know one large firm has applied to an establishment in Glamorganshire for calamine-brass. Perhaps the difference between the two kinds of brass would not now be found, if the manufacture of calamine-brass were resumed; and that which formerly existed may have depended upon inferiority in the quality of the zinc produced at that time. Calamine-brass, I believe, ceased to be manufactured in Birmingham because its price was sensibly higher than that of common brass.

I have met with a statement to the effect that a Mr. Champion obtained a patent, about the year 1818, for making brass by exposing plates of copper to the vapour of zinc *below* the melting-point of brass;[3] but in the Abridgments of Specifications relating to Metals and Alloys, I do not find any record of this patent. It has been supposed that the remarkably malleable brass of Nuremberg was produced by a similar method.

Direct preparation of Brass.

This is effected either in *crucibles*, as in ordinary brass-foundries, or in *reverberatory furnaces*, as in the manufacture of yellow-metal sheathing. The crucibles employed for this purpose have been previously described. The zinc is gradually and cautiously added to the copper when the latter has *just* melted. The ingots of copper, before being put into crucibles, should be heated to redness. The furnaces in use in Birmingham are about 10 inches square and 2 feet deep, while those which I have seen in London are round. The flue leading to the stack should be *small*, and close to the top of the furnace; but its size must obviously vary with the stack and other conditions. The fuel should be *good* coke, and not such as frequently contains a large quantity of corrosive ash. The metal, when well melted, is skimmed and poured into sand-moulds for castings of various kinds; or, when intended for rolling, into closed iron ingot-moulds, previously warmed, lightly oiled and dusted over with charcoal in the interior. In former times moulds of granite were used for casting ingot-brass. In the making, casting, and remelting of brass, there is always an inevitable loss from the volatilization of zinc, for which a due allowance is made to the founders when they deliver the metal.

The Chinese appear to be unacquainted with the art of rolling brass, and, as substitute, cast it into tolerably thin sheets. I have a specimen of one of these, rather exceeding $\frac{1}{16}$ inch in thickness, which I received from my friend Harry S. Parkes, so well known in his official capacity in China. It has been analysed in my laboratory by Mr. T. Philipps, and found to have the following composition:—

Copper	56·59
Zinc	38·27
Lead	3·30
Tin	1·08
Iron	1·47
	100·71

[3] Manuels-Roret. Alliages Métalliques, Paris, 1839, p. 169.

Muntz's metal.—This alloy, and its application "for sheathing the bottoms of ships and other such vessels," was the subject of a patent granted to the late George Frederick Muntz, of Birmingham, in 1832.[4] The proportions specially recommended in the specification are 60 per cent. of copper and 40 of zinc; but these proportions may be varied from 50 up to 63 per cent. of copper, and from 50 down to 37 per cent. of zinc. Best-selected copper and foreign zinc are directed to be used. The metal is cast into ingots and rolled *while hot* into sheets, which, when finished, are "pickled" in sulphuric acid diluted with water to free them from adherent scale, and afterwards washed in water. In the same year Mr. Muntz obtained a second patent for "an improved manufacture of bolts and other the like ships' fastenings."[5] Precisely the same proportions of copper and zinc are claimed in this patent as in the first. In 1846 a third patent was granted to Mr. Muntz for the use of an alloy consisting of 56 per cent. of copper, 43¼ of zinc, and 3¾ of lead.[6] In the specification it is directed that only the purest metals should be used, and that the alloy is to be cast into ingots, which are to be rolled at a red heat, and treated in other respects in the manner stated in the specification of the first patent. I am not aware whether the alloy last described has ever been manufactured and applied; but my impression is that it has not; and I shall, therefore, dismiss it from further consideration. I may state that I have succeeded in rolling brass well, which, on subsequent analysis, was found to contain not less than 8 per cent. of lead.

The theory assigned by Mr. Muntz for the application of his alloy is, that by exposure to sea-water the zinc is slowly and uniformly corroded over the entire surface, whereby the attachment of barnacles, &c., is prevented. Mr. Faraday informed me that in a specimen of sheathing formed of the alloy in question, which had long been exposed to the action of sea-water, he found no zinc remaining. Experience, especially of late, has certainly not confirmed the statement concerning *uniformity* of corrosive action, as much of the modern sheathing is eaten away in holes, notwithstanding the declaration of copper smelters that in the manufacture of yellow metal they employ only *best-selected* copper and zinc of the best quality!

Muntz's metal, or yellow-metal sheathing, has entirely superseded copper-sheathing in the merchant service, though the latter is still retained in the Navy. Its special advantages are stated to be, that it keeps the bottoms of ships cleaner and costs considerably less than copper-sheathing.

It is now generally made in reverberatory furnaces, the zinc being cautiously added to the melted copper. The melted metal is tapped into a vessel lined with clay, out of which it is laded into suitable closed iron ingot-moulds, the interior of which has been lightly oiled and dusted over with charcoal in the usual manner. Just previously

[4] A.D. 1832, Oct. 22. No. 6325. Abridgments of Specifications relating to Metals and Alloys.

[5] A.D. 1832, Dec. 17. No. 6347.

[6] A.D. 1846, Oct. 15. No. 11410.

to tapping, samples of the alloy are taken out, in the same manner as copper-proofs in the process of refining copper, and cast into small ingots, which are passed through rolls while still hot, and are afterwards broken across, when, if the fracture presents the proper appearance, the metal is tapped out forthwith. The fracture should be close and finely granular; but if it does not present the proper appearance, zinc is thrown into the furnace and well mixed with the alloy, after which the fracture is again examined, and if it is right, lading takes place immediately; but if not, the process of adding zinc and the testing of the fracture must be repeated until the desired quality is attained. The eye of the furnace man requires to be educated for this kind of examination. Although the proper quantities of the two metals may have been put into the furnace in the first instance, yet, from the very nature of a reverberatory furnace, it is impossible to calculate upon the precise amount of zinc which may be volatilized, even in the same furnace at different periods. Hence the necessity of the testing, &c. above described. But as the usual charge of a furnace consists of copper, "new scrap," and old yellow sheathing, of which the average composition is not exactly known, it becomes all the more necessary to follow the course above described in order to produce an alloy of the right quality. I am informed by an experienced yellow metal manufacturer, that the proportion of zinc should not exceed 38 per cent.—that if it sensibly exceeds this proportion, the sheathing is apt to become friable—and that if it is sensibly below this proportion, it wears away too rapidly.

The rolled sheets, after final annealing, are immersed in dilute sulphuric acid, scoured on the surface with flannel and sand, and afterwards washed and dried.

I am assured that cast yellow-metal nails of the same composition as the sheathing cannot be used for attaching it to the bottoms of ships. The copper sheathing in the Navy is attached by nails having the following composition:—

Copper	86·82
Tin	9·30
Zinc	3·88
	100·00

Mr. Muntz, like most successful patentees, had to encounter opposition on the part of certain copper-smelters, and to defend his patent-rights in the Courts of Law. He succeeded in obtaining a signal victory over his opponents, which certainly has not always been the fortune of patentees who have benefited either themselves or the world by their inventions. At the expiration of the patent in the ordinary course of 14 years, Mr. Muntz applied to the Privy Council for an extension of it, when he admitted, if I remember correctly, that it had yielded him a profit of not less than 68,000*l.* The application was refused. A few years afterwards Mr. Muntz died, and his property was sworn under 600,000*l.*! The manufacture of the alloy is still conducted on a very large scale near Birmingham, by one or more of his

sons. There are but few if any metallurgical patents which have been so profitable to the patentee as that of Mr. Muntz. Most of the large copper-smelters are now engaged in the manufacture of Muntz's metal.

Miscellaneous Observations on Brass.

Brass intended for rolling.—It is stated, and I believe correctly, that the presence of antimony is especially injurious to brass intended for rolling, as it renders the metal brittle and very liable to crack.

Brass intended for turning.—It is usual to introduce a small quantity of lead into brass intended for this purpose, in order that the turnings may "leave the tool easily." About 3 ozs. of lead are added to 10 lbs. of brass; and this addition should be made after the crucible containing the melted brass has been taken out of the furnace for casting, the metal being afterwards well stirred. Chaudet gives the following analysis of brass fit for lathe-work and filing:—[7]

Copper	65·80
Zinc	31·80
Lead	2 15
Tin	0·25
	100·00

The tin is supposed to be accidental.

Brass for engraving upon.—A little tin is a good addition to brass intended for door-plates, as it gives crispness, and causes the metal to "break up short" under the graver.

Brass for the use of braziers.—It should not contain less than 66½ per cent. of copper.

Composition of a variety of brass from Paris.—It was exhibited in the Paris Exhibition of 1855; it was in the form of an ordinary table-spoon, and was thinly electro-plated with gold, which peeled off under the action of nitric acid; the surface of a portion was completely removed by filing, and the remainder analysed in my laboratory by Mr. Burbidge Hambly: it had the following composition:—

Copper	87·83
Zinc	12·44
Iron	0·35
	100·62

Electro-deposition of brass.—This is now extensively practised in Birmingham.

Molecular changes in brass.—Some kinds of brass wire become extremely brittle in the course of time, especially if subjected to vibration. I have seen thick brass wire become almost as brittle as glass in the course of a few weeks, after having been kept extended and subjected to vibration. Brass chains used to support objects, such as chandeliers, &c., have been known to lose their tenacity, become brittle, and

[7] Manuel de l'Essayeur, p. 370.

break without any assignable cause. Ship bolts of Muntz's metal are sometimes found to undergo a singular kind of exfoliation, the metal on the exterior becoming separated, more or less completely, into concentric laminæ, from a solid cylindrical nucleus within. Mr. Clifford, of Birmingham, has remarkable examples of this change. It affords me great pleasure to acknowledge the kindness which I was accustomed to receive from this gentleman during my residence in Birmingham. His rolling-mill was at all times accessible to me for the purpose of testing the rolling qualities of any metallic substances in the examination of which I might be engaged.

Annealing brass-wire.—Some wire-drawers state that, if brass-wire is subjected to the process of annealing, immediately after it has been taken off the drum on which it has been wound during the process of wire-drawing, it will fly to pieces; whereas another experienced brass manufacturer assured me that this is only true of brass wire consisting of 75 per cent. of copper and 25 of spelter. This effect is prevented by subjecting the coil of wire, after its removal from the drum, to strong concussion by seizing one part of the coil with the hands, raising it, and heavily striking a bench with the other part, repeating the process several times.

Defects in the casting of brass.—Minute cavities occasionally exist here and there on the surface, which are so small as to escape detection by the eye. They are, probably, caused by minute bubbles of air, and in some cases appear to be immediately *below* the surface, only becoming opened externally during the processes of filing, turning, &c., and forming as it were little culs-de-sac. Cavities of this kind doubtless cause what is termed "spuey metal," that is, brass upon the surface of which *after* lacquering spots of green efflorescence make their appearance in the course of a short time. It is easy to conceive that in dipping the acid may penetrate some of these cavities and not be completely removed during the subsequent washing in water, so that nitrates of zinc and copper would remain in them and eventually occasion the efflorescence in question.

Lacquer.—That commonly employed is made by dissolving shell-lac in proof-spirit, and colouring with the resinous substance called *dragon's blood.* The lacquer heightens the colour of brass, or renders it more golden in tint. Lacquer may be pale or deep in tint, when it is known as pale or bronze-lacquer, or it may be variously coloured. A transparent colourless lacquer is a desideratum for German silver. A substance called bleached shell-lac is sold, and, I believe, used for very pale lacquer. The lacquer is warmed and brushed over the article, which has been also previously warmed on stoves. If the temperature is too cold, a dulness of surface is produced which is not removed by re-heating. The surface of brass is frequently coloured or *bronzed* after "dipping" and before lacquering. A dark grey coating is produced by dipping the article in a solution of arsenious acid in hydrochloric acid—by applying a dilute aqueous solution of bichloride of platinum—by applying an aqueous solution of corrosive sublimate mixed with vinegar—or by rubbing plumbago over the

surface. By the application of lacquer to the surface of brass which has received a dark grey coating by any of these processes, a bronze-like tint is produced, due to the light reflected through the coloured stratum of varnish produced by lacquering from the bright surface underneath. Precisely the same effect may be obtained by rubbing plumbago over a piece of writing paper and then lacquering the surface as in the case of brass.[8] For common work the corrosive sublimate method is extensively used; it is said to cause trouble when it comes in contact with soft solder, with which the reduced mercury amalgamates. The platinum process is used for instruments, such as theodolites, levels, &c.; and in these the bronze is much blacker, as pale is employed instead of yellow lacquer. These methods I know are employed, and probably there may be many others. The beautiful colours of brass foils are communicated by variously coloured lacquers. The coating of resinous matter adheres with remarkable tenacity, and is not detached by bending the foil backwards and forwards repeatedly. The manufacture of these foils is, I believe, quite an art, and formerly there was only one person in Birmingham who knew how to practise it successfully.

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[8] I have much pleasure in acknowledging my obligation to Mr. A. C. Hedges for information concerning this and some other points relating to lacquering.

APPENDIX.

The following analysis of an extremely bad sample of copper-sheathing, from H.M.S. "Fantome," has just been completed in my laboratory by Mr. C. Tookey. It was put on at Chatham in March, 1844, and taken off in December of the same year. It was marked "New Cake Copper, N." The loss per sheet per annum was at the rate of 5·62 oz. The sheathing was irregularly corroded in patches, where it was eaten away in holes, while other portions remained sound and free from corrosion :—

	Per cent.		Per Ton. lbs.	oz.	grs.
Lead	0·1187	...	2	10	234
Bismuth	0·1240	...	2	12	193
Antimony, with a trace of Tin	0·0143	...	0	5	52
Arsenic	0·1908	...	4	4	167
Iron	0·0042	...	0	1	221
Nickel	0·0287	...	0	10	128
Phosphorus	None.				

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